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1.—SOME MEASUREMENTS OF THE BRIGHTNESS OF VARIOUS PARTS OF THE SKY BY MEANS OF A RECTIFIER PHOTO-ELECTRIC CELL. By H. H. Poole, sc.d., and W. R. G. Atkins, sc.d., f.inst.p., f.r.s.

2.—SOME DIFFICULTIES IN CURRENT VIEWS OF THE THERMAL HISTORY OF THE EARTH. By J. H. J. Poole, sc.d.

3.—ABNORMAL CONES OF *FITZROYA* AND THEIR BEARING ON THE NATURE OF THE CONIFER STROBILUS. By Joseph Doyle, Botany Department, University College, Dublin, and Mary O'Leary, Assistant in the Department. (Plate 1.)

4.—A NOTE ON THE MOLECULAR COMPLEXITY OF AMYLOSE IN POTATO STARCH. By J. Reilly, m.a., sc.d., P. P. O'Donovan, ph.d., and Miss H. Murphy, m.sc., University College, Cork.

5.—THE OXIDATION OF HYDRAZINE BY POTASSIUM FERRICYANIDE. Part I: THE INFLUENCE OF GASEOUS SUPERSATURATION ON THE MEASUREMENT OF REACTION VELOCITY. Part II: THE REACTION IN PRESENCE OF ACETONE. By Thomas Norman Richardson, m.sc., and Kenneth Claude Bailey, sc.d., litt.d., Fellow of Trinity College, Dublin.

[*Authors alone are responsible for all opinions expressed in their Communications.*]

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THE

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THE ROYAL DUBLIN SOCIETY.

No. 1.

SOME MEASUREMENTS OF THE BRIGHTNESS OF VARIOUS PARTS OF THE SKY BY MEANS OF A RECTIFIER PHOTO-ELECTRIC CELL.

By H. H. POOLE, Sc.D.,

AND

W. R. G. ATKINS, Sc.D., F.Inst.P., F.R.S.

[Read November 28, 1933. Published separately December 28, 1933.]

An account has been given in a previous paper (9) of some tests of various rectifier cells, which showed that the Bergmann selenium cell manufactured by the Weston Electrical Company was apparently very suitable for the measurement of daylight in the field. This cell has since been used for various daylight readings, including estimates of the colour variations in shaded sites and under water, accounts of which will be given elsewhere. The present paper records its use for the measurement of the light received from small areas of sky, from which it is possible to estimate the average altitude of the diffuse light received from the entire sky, and hence the ratio of the vertical illumination, as recorded by a photometer with a horizontal window of diffusing glass, to the total diffuse illumination at an open site.

In comparing the results given below with the numerous measurements of sun and sky radiation made by Abbot, Fowle, and Aldrich, at Mount Whitney and elsewhere (2, 3, 4) it must be remembered that these workers measured the total radiation transmissible by glass, while the present measurements were made with a cell whose colour-sensitivity curve is not unlike that of the eye. Some of the skies studied by Abbot, Fowle, and Aldrich, were evidently much clearer than any that we observed, but the general nature of the results is similar.

The cell had been standardised, both with and without an opal glass diffusing window, against an open carbon arc, by the method which we have always used for emission cells, whose colour-sensitivities generally differ so greatly from that of the eye as to render their standardisation by any of the usual sources almost meaningless (8). This objection does not apply to the

Weston cell, as its colour-sensitivity curve is so like that of the eye that a subsequent test with a sub-standard filament lamp at a colour temperature 2360° K. gave a result only differing by 5 per cent. from that obtained with the arc. In the results given below the arc standard has been adopted. The scale of values, accordingly, differs somewhat from those of all our previous results, which were based on the daylight readings of a blue-sensitive potassium vacuum cell standardised against the arc.

The cell, whose effective diameter is 4 cm., was mounted in place of the mirror in an old reflecting telescope, the open end of which was 12·64 cm. in diameter and at a distance of 83·5 cm. in front of the cell. The semi-angle of the cone of light falling on the cell was thus 4·3°, the solid angle being 59·2 square degrees. The maximum penumbral semi-angle was about 6°, so that with the telescope set at an elevation of 7½°, the lowest regularly used, the horizon was not in the field of view of any part of the cell.

For observations on direct sunlight a thin wooden diaphragm was fitted on the open end of the tube with a central aperture 8·77 cm. in diameter. Thus, when the tube was pointed directly at the sun (as indicated by the attached finder telescope, which was fitted with a translucent paper screen in place of the eye-piece), the cell was completely illuminated by direct sunlight, which, however, was completely shaded from the internal wall of the tube. It was possible to verify this, and to confirm the accuracy of the setting, by carefully looking down the tube. For sunlight measurements an opal glass whose transmission factor was known was mounted immediately in front of the cell in order to reduce the illumination of the latter to a convenient value. This glass was removed for sky measurements with the cell in the telescope tube.

It was found that with the open tube a considerable correction was needed to allow for the effect of light reflected from the tube walls (which were blackened inside), even when all direct sunlight was shaded off from the open end, as was always done in making sky measurements. This correction was estimated by making observations on the same area of sky, first with the diaphragm in place and two additional stops at suitable positions inside the tube to cut off internal reflections, and immediately afterwards with the fully open tube. The mean of such measurements gave a value 2·89 times as great with the open tube. As the effective solid angle with the smaller stop, with which the internal reflection must have been very small, was 28·5 square degrees, the ratio must have been increased from 59·2/28·5, i.e. 2·08, to 2·89 by reflection. In plotting the results given later the values obtained with the open tube on June 7th, 8th, and 9th, have been divided by 1·39 to allow for internal reflection.

The results for July 3rd were obtained with the stops in position. This obviates uncertainty as to the size of the reflection correction, but renders some of the readings unduly small.

The current was measured with a Cambridge Unipivot 'Versatile' galvanometer of 10 ohms resistance giving 0·5 scale division per microampere,

which had been standardised recently. For measurements of sunlight and full sky light this was shunted by suitable parallel and series resistances to give suitable deflections while maintaining the resistance of the galvanometer circuit very close to 10 ohms. The need for this precaution has already been pointed out (9), but the special shunt made for this purpose was not available in Dublin. A more sensitive instrument would be better for measuring the light from small areas of sky, and for such small illuminations a higher resistance winding could be used, but for all-round daylight measurements this low-resistance instrument is very suitable. The smallest reading, obtained on July 3rd with the diaphragm, for a very clear North sky, was about 1·5 scale divisions. This could be read with a lens to about 0·1 scale division, and the variation in the zero, as noted by darkening the cell at frequent intervals, was about the same amount.

In deducing the illumination from the current it was necessary to correct for the curvature of the current: illumination curve, found as described in the previous paper (9). It was found that this could be done with sufficient accuracy by dividing the current in microamperes, C, flowing through a 10-ohm galvanometer by $1 - 0{\cdot}003 \times \sqrt{C}$, the use of a divisor in place of multiplying factor being more convenient in this instance for slide rule working. From the corrected current in μa the corresponding normal illumination in meter candles could be found by multiplying by 5·93 or by 13·56, according as the cell was bare or covered with opal glass, respectively. This divided by the solid angle of the field of view of the telescope gave the illumination per square degree, in the case of the narrow-angle sky light measurements. For readings with the photometer window horizontal the opal window was always used, and, although its diffusing properties are excellent, the apparent vertical illumination must be further corrected for the increased reflection-loss at the surface of the window caused by the obliquity of the light (7). The readings of the total diffuse sky light have, accordingly, been multiplied by 1·06, the obliquity correction calculated for a uniform sky, for which the average altitude of diffuse illumination is 30°. It will be seen that for a blue sky the average altitude is really lower, while for a cloudy sky it is higher than 30°. The correction used is, therefore, not quite exact. The obliquity correction for pure sunlight of altitude 45°–60° is only 1·005 to 1·01; this small correction was also applied.

The measurements were made on the roof of the Royal Dublin Society's buildings at Ballsbridge (Lat. 53° 20′ N., Long. 6° 14′ W.) about 2 miles east of the centre of Dublin. The exposure in all directions was almost perfect, and on the days in question there was little local smoke noticeable, none being visible at high altitudes (say over 30°). The total effective vertical illumination was first measured, the opal glass being in place on the cell, which was accurately levelled. Direct sunlight was then screened off by means of a card about 20 cm. × 16 cm. held on the end of a long rod at about 2 m. from the cell so that its shadow covered the latter. This gave the value of the effective vertical

illumination due to diffuse light from the sky. The card in this position blocked out about 25 square degrees of sky in addition to the sun. With a clear sky the light from this area was only just appreciable (compared with the full sky light), as was found by holding the card so that its shadow fell just clear of the cell. The effective vertical illumination due to the sun was found by difference. The actual vertical illuminations V_s and V_d due to sunlight and diffuse sky light, respectively, were found by multiplying the effective values by the corresponding obliquity factors. V, the total vertical illumination, equals $V_s + V_d$. Readings with the cell alternately shaded and fully exposed were made alternately and the mean taken. We have always used the symbol β to represent the ratio V/V_d. It is a convenient index of the relative intensity of the sunlight, but its value obviously depends on the colour sensitivity of the cell used. Thus the values recorded below are much higher than would have been recorded by a blue-sensitive potassium or sodium cell under the same conditions (5, 6).

The cell was then mounted in the telescope with diaphragm and opal glass, and a reading of the direct sunlight I_s was taken. Evidently V_s should be equal to $I_s \sin a$, where a is the sun's altitude. The accordance here was always quite satisfactory. The opal glass was then removed, and readings taken for various parts of the sky, direct sunlight being carefully screened off the aperture of the tube. This is necessary in order to avoid the large errors that would otherwise be caused by internal reflection of the sunlight, but it is evidently essential that the screen should be outside the field of view of any part of the cell, so that even with the diaphragm in use reliable readings could not be taken within about 8° of the sun.

Each azimuth setting was made by aligning the telescope tube with some distant object which had just been chosen as being at the required angle east or west of the sun. Measurements in this azimuth were then made, at altitude intervals of 7½°, from 7½° to 90°. This usually took about 6 minutes, during which time the sun moved 1·5°. Equal E. and W. azimuths were done successively, and their means have been plotted in the graphs in Figs. 1 and 2.

At the conclusion of the sky measurements the opal glass was replaced, and readings taken of I_s, V_s, and V_d.

In plotting the results, the values obtained at identical azimuths E. and W. of the sun have been averaged. Thus, the 0° and 180° graphs each represent a single set of measurements, but each of the others gives the mean of two sets. No other attempt at smoothing has been made, the graphs being obtained by joining the individual points (at 7½° altitude intervals) by straight lines.

It is interesting to compare the results obtained by integrating the measurements over various parts of the sky with those found directly for the entire diffuse vertical light, and this has been done in each case. The agreement is probably as good as one could expect in view of the facts that (*a*) it is difficult to estimate the light received from the regions close to the sun, especially on June 8th, when no readings were made at moderate azimuths, and

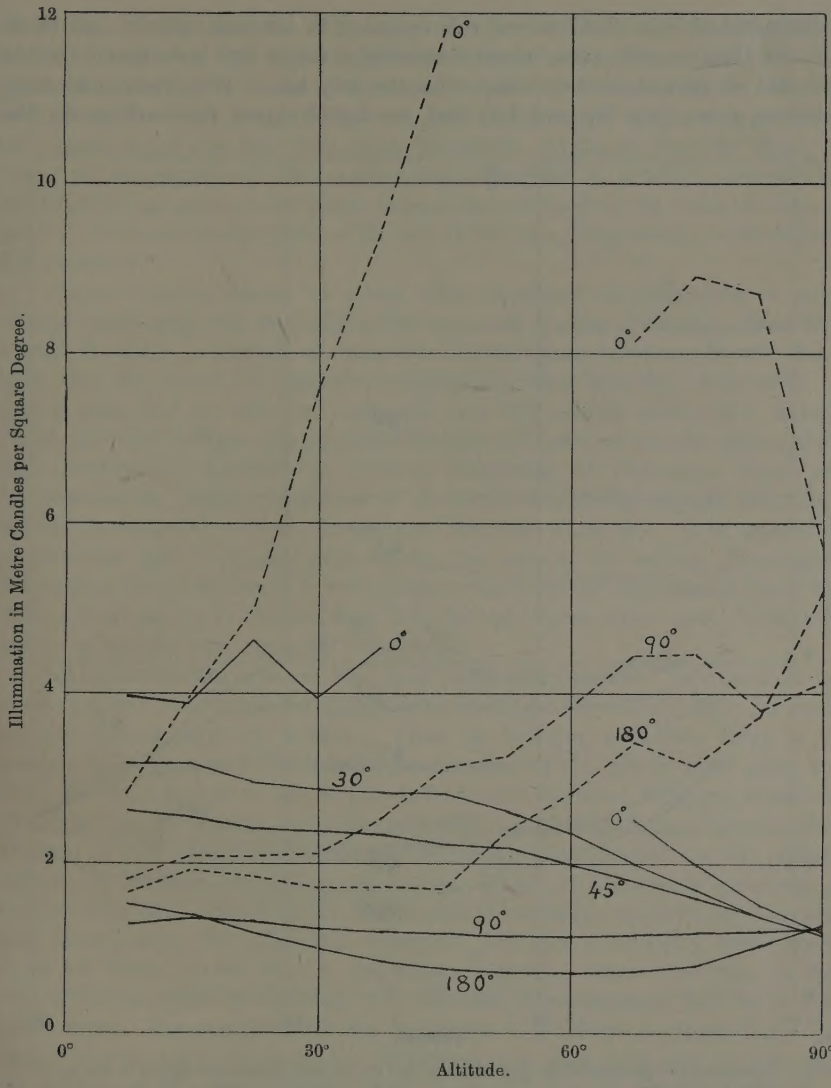

FIG. 1.—Variation of brightness of the sky with altitude for various azimuths relative to that of the sun.

Dotted graphs, June 8th, 1933, 11·13–11·38 G.M.T.; α, 57–58°: sky almost covered by light cloud; wind N. Initial and final readings of sunlight and full sky light in thousands of meter candles gave:—

At 11·01–11·09 G.M.T.; α, 56°; V, 64·3; V_d, 46·8; V_s, 17·5; β, 1·4; I_s (varying rapidly), 17–35; $I_s \sin \alpha$, 14–29.

At 11·41–11·43 G.M.T.; α, 59°; V, 81·8; V_d, 48·3; V_s, 33·5; β, 1·7; I_s (varying), 30; $I_s \sin \alpha$, 26.

By integration from graphs we find V_d, 40·2; I_d, 67·0; V_d/I_d, 0·60; average altitude of diffuse sky light, 37°.

Continuous graphs, June 9th, 1933, 14·40–15·24 G.M.T.; α, 50–45°; blue sky, few light clouds; wind N. Initial and final readings:—

At 14·33–14·36 G.M.T.; α, 51°; V, 76·4; V_d, 15·5; V_s, 60·9; β, 4·9; I_s, 78·8; $I_s \sin \alpha$, 61·3.

At 15·29–15·31 G.M.T.; α, 44°; V, 63·5; V_d, 17·4; V_s, 46·1; β, 3·6; I_s, 64·3; $I_s \sin \alpha$, 44·6.

From graphs V_d, 16·7; I_d, 35·3; V_d/I_d, 0·473: average altitude of sky light, 28°.

the presence of light cloud caused this region to be intensely bright, and (*b*) it is known that the opal glass, whose transmission factor had been found for arc light, has an appreciably lower factor for the deep blue. With clear blue skies, therefore, as on June 9th and July 3rd, we should expect the readings for the

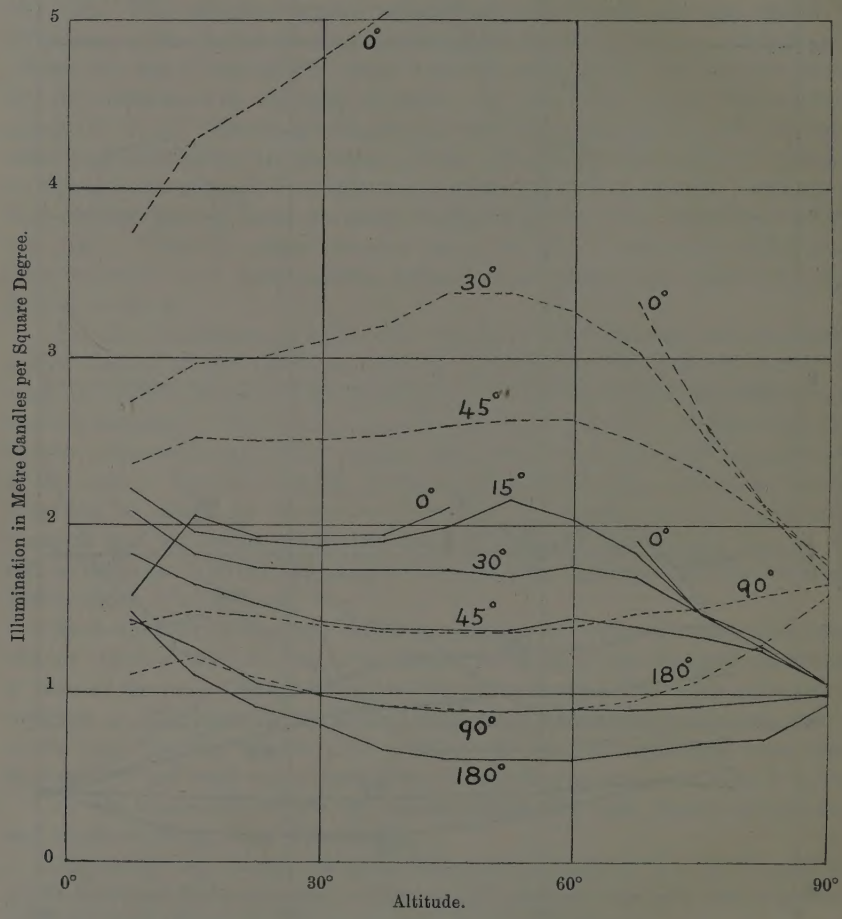

Fig. 2.—Variation of brightness of the sky with altitude for various azimuths relative to the sun :—

Dotted graphs, June 7th, 1933, 10·05–10·33 G.M.T. ; α, 50–53° ; hazy blue sky, some very light clouds ; wind E. Initial readings of sunlight and full sky light in thousands of meter candles gave :—

At 9·58–10·03 G.M.T. ; α, 49° ; V, 67·9 ; V_d, 22·4 ; V_s, 45·5 ; β, 3·0 ; I_s, 60·2 ; $I_s \sin \alpha$, 45·4.

By integration from graphs we find V_d, 19·1 ; I_d, 37·6 ; V_d/I_d, 0·508 ; average angle of diffuse sky light, 30·5°.

Continuous graphs, July 3rd, 1933, 11·23–12·33 G.M.T., 57–60° : very clear blue sky, no clouds but a little scattered smoke at times ; wind N.E. Initial and final readings :—

At 11·14–11·20 G.M.T. ; α, 57° ; V, 84·2 ; V_d, 10·9 ; V_s, 73·3 ; β, 7·7 ; I_s, 90·1 ; $I_s \sin \alpha$, 75·6.

At 12·38–12·42 G.M.T. ; α, 60° ; V, 86·2 ; V_d, 10·4 ; V_s, 75·8 ; β, 8·3 ; I_s, 90·0 ; $I_s \sin \alpha$, 77·8.

From graphs V_d, 11·4 ; I_d, 25·4 ; V_d/I_d, 0·449 ; average altitude of sky light, 27°.

whole sky obtained with the diffusing glass to be slightly lower than the values found by summing the light from individual regions as found with the bare cell. On July 3rd with the diaphragm in place it was possible to take sky measurements rather closer to the sun, and the clearness of the sky prevented the region round the sun from being excessively bright, so that the effect (*a*) above was less important. When allowance is made for (*b*) it will be seen that the agreement is as good as one could expect, and shows that the same cell can be used to compare illuminations of 20 and 10,000 m.c., respectively, with at least fair accuracy.

Figure 1 gives results for a day with an almost uniform layer of cirro-stratus cloud over the sky (June 8th) and for a clear blue sky (June 9th). Figure 2, which is plotted on twice the vertical scale, compares results for a hazy blue sky (June 7th) and an exceptionally clear blue sky (July 3rd). It will be seen that the effect of haze, and to a still greater extent that of light cloud, is to (*a*) increase the illumination from all parts of the sky above about 10° altitude, (*b*) increase the relative proportion of high-angle light, and (*c*) increase the relative brightness of the sector containing the sun, and hence greatly increase the vertical illumination from the whole sky. It is interesting to note that for a perfectly uniform sky the ratio of the vertical illumination V_d to the total illumination I_d is 0·5, the average angle of illumination being 30°. With a clear sky V_d/I_d was less than this, the light being more nearly horizontal, while the reverse was true with a cloudy sky.

No measurements have yet been made with heavy clouds. It is obvious that under a heavy rain-cloud the illumination would be very small, while its sunlit surface may be intensely bright. There is, however, a definite limit to the possible brightness, as it can readily be seen that if the albedo were unity, i.e., if all the light falling on the upper surface were scattered back the brightness would be I/π per square radian or $\pi I/(180)^2$, i.e., $I/10{,}313$, per square degree, where I is the normal component of the illumination incident on the surface. Abbot and Fowle's estimate of the average albedo of the clouds examined by them is 0·65 (1). Since I might, on the scale of values in use here, be something like 110,000 m.c., the maximum brightness, even for a perfectly white cloud, could not much exceed 10 m.c. per square degree, a figure very close to that found for the light transmitted, but scattered through about 12° by a light cloud layer. For actual clouds the brightness is unlikely to exceed 7 m.c. per square degree, about 10 times the brightness of a deep blue sky, or 3·5 times the brightness of a candle flame, which is about 2 m.c. per square degree.

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No. 2.

SOME DIFFICULTIES IN CURRENT VIEWS OF THE THERMAL HISTORY OF THE EARTH.

By J. H. J. POOLE, Sc.D.

[Read November 28, 1933. Published separately January 26, 1934.]

Professor Arthur Holmes in a recent paper (1) has given a very useful summary of the present position as regards the various theories which have been advanced to explain the probable thermal history of the earth. Of these theories there can be no doubt that the "contraction hypothesis" so ably supported by Jeffreys presents to a physicist much the least difficulties, if the perfectly plain assumptions as to the distribution of radioactive elements in the earth are once granted. This arises from the fact that all heat transference takes place by conduction, and we are not troubled by either convection currents or change of state of the medium. Unfortunately some geologists are not prepared to grant the rather stringent conditions necessary for the truth of the theory, and accordingly various attempts have been made to develop some theory which would take into account the effects of the two latter factors, if the distribution of radioactivity is not assumed to be that necessary for the contraction hypothesis. The original theory of this nature was put forward by Joly (2). It is characterized by the fact that it is only at certain epochs that convection currents in the earth are large, and these currents are always restricted to a comparatively shallow surface layer of the order of, say, 200 km. thickness. Holmes (3) has proposed a modified theory in which convection currents are supposed to be acting continually, and may reach to very great depths in the earth. It is with some of the problems inherent in this theory that I propose to deal. It must be understood, however, that only very tentative conclusions can be reached, owing to our great ignorance of the real properties of the medium at the temperatures and pressures involved.

In most current theories it is assumed, as Holmes points out, that the earth began its thermal history as a liquid globe. Cooling then proceeded very rapidly at the surface, the inner layers being cooled by convection currents. No complications occur till the medium reaches its freezing point at some place. It is to be remarked that as long as the upper surface is a liquid, the cooling by convection currents will be so rapid that the effect of the radioactive generation of heat is entirely negligible. It is only when we get a thermally insulating layer of solid material that radioactive heating becomes important.

In the solidification of a liquid cooled at the top two quantities are important. These are the adiabatic or convection gradient and the freezing point gradient with pressure. In a column of cooling liquid the temperature

gradient downwards will never exceed by any large amount the convection gradient, and from this it follows that if the freezing point gradient is greater than the convection gradient, a liquid column cooled at the top will solidify at the bottom, as originally pointed out by Lord Kelvin. This condition is apparently fulfilled by the materials of which the outer layers of the earth are composed (4 and 5). If x is the depth from the top of the column and θ the temperature at this depth, the convection gradient of temperature $A = \frac{\theta \alpha g}{\sigma}$, where α = coefficient of thermal cubical expansion and σ = specific heat of medium, both at constant pressure. The freezing point gradient B is given by the expression $\frac{gT}{L}\left(1 - \frac{V_1}{V_2}\right)$ where T is the freezing point, L the latent heat of fusion, V_1 and V_2 the specific volumes of the solid and liquid, respectively. For small pressures, i.e., small depths, B is greater than A. The effect of increasing pressures is undoubtedly to decrease the ratio of B to A, so that at some depth, probably of the order 200 to 400 km., $B = A$. This is generally accepted. Below this depth there are two possibilities. $\frac{B}{A}$ may further decrease, which is the simplest assumption, or $\frac{B}{A}$ may increase again as Holmes claims in his convection theory. I do not consider that this assumption is necessary for his theory, in fact I think it invalidates it.

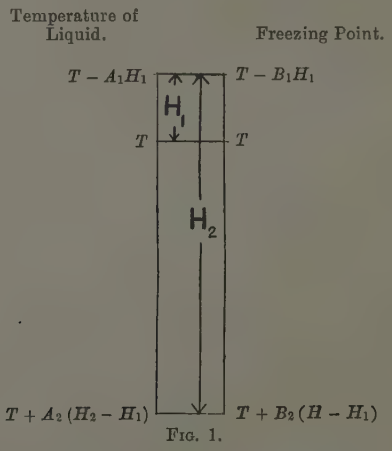

FIG. 1.

Let us consider a column of a uniform medium for which $B > A$ for depths less than H_1, $B = A$ for depth H_1, and $B > A$ for depths greater than H_1. Furthermore, let us assume that the freezing point is first reached by cooling at the top at the depth H_1. The conditions will then be as shown in Fig. 1. It is assumed that the effect of the convection is to ensure that the convection gradient will be maintained both above and below H_1. Thus

the actual temperature at the surface is $T - A_1 H_1$, and at the bottom $T + A_2(H_2 - H_1)$ where H_2 is total depth of column. The corresponding freezing points are, at the surface $T - B_1 H_1$, at the bottom $T + B_2(H_2 - H_1)$. A_1 is the average convection gradient above H_1, and A_2 the average convection gradient below H_1, B_1 and B_2 having similar significances for the freezing point gradients. Now on Holmes' assumption:

$$B_1 > A_1$$
$$B_2 > A_2$$
Hence $$T - A_1 H_1 > T - B_1 H_1$$
and $$T + A_2(H_2 - H_1) < T + B_2(H_2 - H_1)$$

i.e., the liquid is above its freezing point by an amount $(B_1 - A_1)H_1$ at the top, and is below its freezing point at the bottom by an amount $(B_2 - A_2)(H_2 - H_1)$. Hence freezing must also be proceeding at the bottom. As a matter of fact under the conditions predicated, freezing will start at the bottom, since the average value of B for the whole column is greater than A, and the freezing point will accordingly be first reached at the bottom of the column. It will then solidify from the bottom upwards in the usual way. If subsequent radioactive heating produces a liquid layer the arguments which have been previously advanced to prove that such a layer tends to move upwards and disappear will still apply, since, for all depths except a narrow zone near H_1, B is greater than A (5 and 6). A layer starting below H_1 will be retarded by the small difference between B and A near H_1 but it will still slowly move upwards till it escapes from this zone. There seems, however, to be no possibility of a permanent convective layer being formed below H_1 since if the top of the layer is in contact with its own solid at the top, its temperature here can only be slightly above the freezing point, and accordingly as already shown its temperature at the bottom would be below the freezing point.

The simpler assumption to make is that for depths less than H_1, $B_1 > A_1$, and for depths greater than H_1, $B_2 < A_2$. Freezing will now start at the depth H_1, the conditions being as shown in Fig. 1. The liquid will be above its freezing point, at the top by $(B_1 - A_1)H_1$, and at the bottom by $(A_2 - B_2)(H_2 - H_1)$ both these quantities being positive by hypothesis. The subsequent history of the cooling of the column depends upon what view we take of the behaviour of the solidified matter forming at H_1.

The adiabatic gradient $A = \frac{\theta \alpha g}{\sigma}$. Now α is positive for nearly all liquids, except water between 0° and 4° C. The specific heat will also be positive. Thus A is positive, and since at depth H_1, $A = B$, B must also be positive at this depth. But

$$B = \frac{gT}{L}\left(1 - \frac{V_1}{V_2}\right),$$

hence the specific volume of the solid must be less than that of the liquid at H_1,

and any solid forming at H_1 would tend to sink. Jeffreys and Holmes, however, hold that the viscosity of the medium would prevent this happening. Let us examine the consequences of this view.

As $B > A$ above H_1 the solidification above this level will proceed upwards very rapidly by cooling at the upper liquid surface, till the whole column above H_1 is solid. If no radioactive material were present the layer below H_1 would now cool excessively slowly by heat conduction through the upper solid crust, the solidification proceeding from the top downwards. Suppose, however, q calories per second are generated per c.c. of medium due to radioactive heating. If q exceeds a very small value the conductivity of the upper solid layer will not be sufficient to carry off the heat from the lower liquid layer, and it will remain in a state capable of convection currents for ever, thus satisfying the condition necessary for Holmes' convection theory.

The distribution of the radioactive matter in the column at this stage is important. In the case of the earth it seems reasonable to assume that as long as it was in the liquid condition there would not be an increasing concentration of the very heavy radioactive elements in the upper layers. Furthermore, the time taken for the solid outer crust above H_1 to form is usually regarded as being very short, being measured in thousands of years. It would seem justifiable, then, to conclude that the original crust would not be richer in radioactive materials than the lower convection layer. The actual experimental measurements, as far as they go, certainly point, however, to a concentration of the radioactive elements in the outer layers. This applies not only to the large difference between granitic and basaltic types, but also to the basaltic types themselves. Thus the basalts from oceanic islands, which are presumably derived from the top of the basaltic layer in the earth, are richer than the continental basalts, which are derived from the deeper layer below the continents. The densities of the basalts also increase with their depth of origin. Dunites and eclogites are still denser and less radioactive (7). Any theory of the earth's thermal history must furnish some plausible explanation of this fact.

This is the difficulty with which the "Contraction Hypothesis" is faced. It seems impossible to imagine that the separation of the radioactive elements, such as demanded by this hypothesis, could have been effected in the very short time necessary for the solidification of the crust down to depth H_1. Now on the contraction hypothesis this crust has never been remelted on a large scale, consequently the lower layer can only have lost its radioactive elements by small local intrusions into the upper solid layer, or by the diffusion of possible volatile compounds of the radioactive elements upwards. Both these processes would be inconceivably slow through a solid crust 200 to 400 km. thick, which is probably the value of H_1. For the "contraction hypothesis" to work it seems necessary to assume that the original crust had practically the same radioactivity as at present. It should be noted that, as already remarked, the small quantities of heat generated by radioactivity will have no effect on the formation of the first crust, as this crust forms from the bottom upwards

and is complete in a few thousand years. I am using the term solidification to mean that the medium has lost the power of transferring matter and consequently heat by convection currents.

Any form of theory, however, which allows either partial or complete refusion of the original outer crust will furnish us with a possible explanation of the observed distribution of radioactivity, as pointed out by Joly and myself. This action, due to the thermal heating of the radioactive elements, is again, however, very slow, and will only have an appreciable effect in a layer of liquid material which is thermally well insulated by an overlying solid non-convective layer. It would have no effect in producing an upward concentration during the primary solidification, as the period is too short. There is no doubt, however, that given a convective layer which persists for a sufficient time, it will produce a concentration of the radioactive elements at the top of the layer. If the top of this layer tends to melt its way upwards, it will carry its extra concentration with it, and thus waves of refusion spreading up from below, and then disappearing, tend to increase the radioactivity of the outer crust at the expense of the lower, as actual measurements demand.

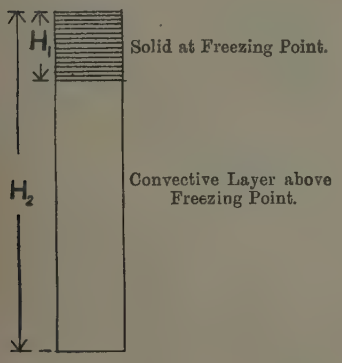

FIG. 2.

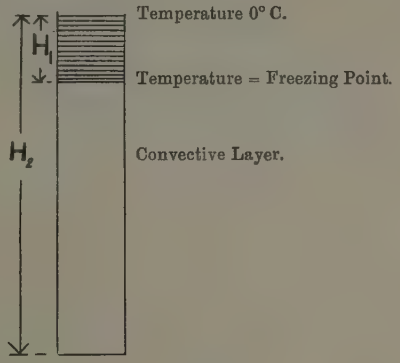

FIG. 3.

Let us now examine rather more closely the conditions which will have to be satisfied for no refusion of the outer primary crust ever having taken place. The conditions at the end of the primary solidification are as shown in Fig. 2. The outer solid now cools by conduction, and the final stable condition is as shown, Fig. 3. It is assumed that the distribution of radioactive elements is uniform. Now the earth is so old compared with the time required for a non-radioactive sphere of the same dimensions to have cooled to its present state, that we must conclude that the present loss of heat by the earth is mainly supplied by the radioactive elements, and not by original heat supplied by cooling. If q is the heat generated per c.c. of medium, the total flow of heat per cm.^{2} at the top of the column is $\int_0^{H_2} q\,dx$. The heat lost per cm.^{2} of the

earth's surface is, however, roughly known from the temperature gradient and heat conductivity of the surface materials. Jeffreys gives the value of $\int_0^\infty q \, . \, dx$ as $2{\cdot}24 \times 10^{-6}$ cal./cm.^{2} sec. (8). Let us take a round value of $2{\cdot}0 \times 10^{-6}$ cal./cm.^{2} sec.

To state the problem clearly we have the following quantities:—

H_2 = total depth of radioactive layer.
A = convection gradient.
B = freezing point gradient.
x = depth.

For $x < H_1$. $B > A$.
For $x = H_1$. $B = A$.
For $x > H_1$. $B < A$.

q = number of calories generated per c.c. per sec.
K = thermal conductivity of solid.
θ = temperature at depth x.
T = freezing point at depth H_1.
θ_0 = surface temperature = 0° C. in final state.
a = surface temperature gradient.

In the final equilibrium state (Fig. 3) the temperature at a depth x in the solid crust is given by the expression

$$\theta = \theta_0 + ax - \frac{qx^2}{2K}.$$

Now
$$Ka = \int q dx = qH_2;$$
$$a = qH_2/K.$$

Also $T = aH_1 - qH_1^2/2K$, since $\theta_0 = 0$,

$$\therefore H_1^2 - 2H_1H_2 + \frac{2KT}{q} = 0,$$
$$H_1 = H_2 \pm \sqrt{H_2^2 - 2KT/q}.$$

Only the value of H_1, which is less than H_2, is admissible.

$$H_1 = H_2\left[\frac{KT}{H_2^2q} - \frac{1}{2}\cdot\frac{K^2T^2}{H_2^4q^2} + \text{etc.}\right].$$

Let us suppose $H_2 = 1000$ km. $= 10^8$ cm. Now $Ka = H_2q = 2{\cdot}0 \times 10^{-6}$. Hence $q = 2{\cdot}0 \times 10^{-14}$. Now $K = 4 \times 10^{-3}$ and $T = 1500°$ C. say.

Hence $\frac{KT}{H_2^2q} = \frac{6}{10^{16} \times 2 \times 10^{-14}} = 3 \times 10^{-2}$; thus higher powers of KT/H_2^2q may be neglected. Finally, $H_1 = H_2 . KT/H_2^2q$.
$= 3 \times 10^6$ cm.
$= 30$ km.

It seems to be highly unlikely that A could be equal to B at such a shallow depth. There is apparently no escape from this conclusion if no remelting is to occur. Thus $H_1 = KT/H_2q$. H_2q is equal to the present rate of loss of heat very nearly on any cooling earth hypothesis, and K and T are approximately fairly well known. This state is a stable one. No redistribution of radioactivity with depth in the lower convective layer will affect it, as this layer will always act as though it had practically infinite thermal conductivity. The only way the stability can be upset is by the transference of radioactive material from the convective to the solid layer. There will be a concentration with time in the upper layers of the convective layer, and possibly by local volcanic intrusions this greater concentration might penetrate into the upper layer. The time for such a process to have produced the present distribution of radioactive elements would seem to be very great indeed. Such a concentration would also permit a further cooling and thickening of the outer crust, but no estimate of the time required can be given, as the ruling factor is the rate at which concentration of the radioactive elements occurs in the upper layer, and this is entirely unknown. The main difficulty with this hypothesis is, however, the very small value of H_1 necessary for its truth, and the only way of avoiding this difficulty is to assume that the original upper layer was much richer in radioactive elements than the substratum.

Suppose we now examine the case in which H_1 has the more probable value of 200 km. the other figures being as before, we see that this will lead to waves of refusion spreading up from below and disappearing again before they reach the surface. The thickness of the lower convective layer is $H_2 - H_1 = 8 \times 10^7$ cm. and the heat generated per cm.^{2} of top surface $= q(H_2 - H_1) = 16 \times 10^{-7}$ cal./sec. If we neglect the radioactivity of the upper solid layer, the amount of heat the convective layer can lose is KT/H_1 cal./cm.^{2}sec. Now if we assume that $T_1 = 2000°$ C., a value which would appear to be quite improbably high, and $K = 4 \times 10^{-3}$, the value found for basalt, then $KT/H_1 = 4 \times 10^{-7}$. Thus the lower convective layer must be accumulating heat and this will lead to melting occurring at the bottom of the solid layer. Fig. 4 shows the condition of affairs when this process has proceeded a distance d upwards. Now the temperature of the liquid at depth H_1 cannot be less than T, and since the liquid is nearly in convective equilibrium, its temperature where it is in contact with the solid will be $T_1 - Ad$. The temperature of the solid is, however, $T - Bd$, and consequently the liquid is hotter than the solid by an amount $(B - A)d$. The loss of heat by the liquid to the solid may be taken as proportional to this excess $= k(B - A)d$. For an ordinary liquid k is about 4×10^{-4}; $B - A$, for the surface basalt, is about 2×10^{-5}, which gives $k(B - A)$ as 8×10^{-9}. In my previous paper on this subject (6) I showed that this value was probably too high for the conditions met with in the earth's crust, and I adopted an arbitrary value of 3×10^{-11} to allow for the high viscosity of the liquid basalt. Near H_1 this quantity will be further reduced owing to A being nearly equal to B, so that we might assume a still lower value for

$k(B - A)$. No experimental data are available, but if we reduce $B - A$ to 1 per cent. of its surface value and take the same value of k as before, we get $k(B - A) = 3 \times 10^{-13}$. Let $(B - A)k = b$ as before. For no change of state to occur in the liquid, the heat lost at the top must equal the heat generated by radioactivity, i.e.,

$$bd = q(H_2 - H_1 + d).$$

For no melting of the solid to take place the heat absorbed by the solid from the liquid must be equal to the heat lost by conduction through the upper solid layer. As an approximation we may take that the heat lost by conduction will be $KT/(H_1 - d)$. In this we assume the temperature gradient in the upper solid to be uniform, and neglect the effect of radioactivity in the solid, and also its rise in temperature due to motion of the freezing point geotherm.

Thus when the liquid is neither losing nor gaining heat,

$$(b - q)d = q(H_2 - H_1).$$

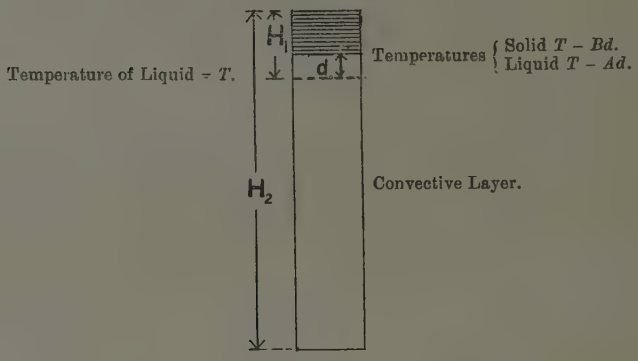

Fig. 4.

Substituting $b = 3 \times 10^{-13}$ and the values of the other quantities previously taken, we find d to be 60 km. approximately. The heat lost by conduction through the solid at this stage is $KT/(H_1 - d) = 5.7 \times 10^{-7}$ calories per sec., and this is much less than the heat gained by the solid from the liquid, which is $(b - q)d$ and is about 17×10^{-7} cals.

Thus the lower surface of the solid layer will continue to melt, thus increasing d and the heat loss of the lower liquid layer. The only possible way for the liquid layer to supply this extra heat is for freezing to start again at the H_1 level. The solid will accumulate again here till transference of heat by convection across the layer is finally prevented. The liquid layer above this partition is now cut off from the heat supply from the lower liquid layer. This upper layer will melt its way up towards the crust and finally disappear as explained in the previous papers (5 and 6). The lower layer will, however, be accumulating heat all the time, and a new wave of fusion will commence, the

whole cycle being repeated. Each refusion will lead to a concentration of radioactivity, till finally we arrive at a stage where the outer layers are much more radioactive than the substratum. If this process is carried far enough it is plain that a state will be reached which will allow a permanently solid crust to be formed down to the depth H_1 or even deeper. Thus the earth at present may satisfy the conditions necessary for the "Contraction Hypothesis," but there must have been a very long period in its history in which it did not. I would again emphasise the fact that any theory which permits convection currents which reach at any time near the surface layers gives a possible explanation of the observed distribution of radioactivity.

There is another point in which the existence of convective layers in the earth introduces difficulties. Jeffreys has made a very clear distinction between a medium which possesses rigidity and one that possesses strength. Briefly a rigid medium will behave as an elastic solid for short period stresses but may yield like a highly viscous fluid to long continued steady stresses. A strong medium will behave as an elastic solid for both. Now a layer capable of having convective currents in it, might possibly be rigid but it cannot be strong. Hence for long applied forces the distribution of stress in the medium must be hydrostatic. Let us consider the conditions that are necessary for the equilibrium of a liquid sphere under its own attraction. If U is the gravitational potential, at a point whose polar co-ordinates are r, θ, ϕ, the condition for hydrostatic equilibrium is that

$$\frac{\partial U}{\partial \theta} = \frac{\partial U}{\partial \phi} = 0,$$

i.e., U is a function of r only. Poisson's equation in polar co-ordinates may be written

$$\frac{1}{r^2}\left[\frac{\partial}{\partial r} \cdot r^2 \frac{\partial U}{\partial r} + \frac{\partial}{\partial \mu}(1-\mu^2)\frac{\partial U}{\partial \mu} + \frac{1}{1-\mu^2} \cdot \frac{\partial^2 U}{\partial \phi^2}\right] = 4\pi\rho.$$

where ρ is the density of the medium and $\mu = \cos\theta$. But since U is a function of r only

$$\frac{\partial U}{\partial \mu} = \frac{\partial^2 U}{\partial \phi^2} = 0,$$

$$\therefore \frac{\partial^2 U}{\partial r^2} + \frac{2}{r} \cdot \frac{\partial U}{\partial r} = 4\pi\rho.$$

Hence ρ must be a function of r only.

No condition as to the form of this function is laid down, and thus solutions in which $\frac{d\rho}{dr}$ is positive are possible. Thus a heavy outer liquid shell might surround a lighter inner core, and be in equilibrium. The equilibrium in this case is obviously unstable, but if the upper layer is truly solid, and thus possesses a finite strength, the equilibrium will be stable. Hence it is possible for a heavy outer solid crust to surround an inner lighter liquid core, the pressure being

hydrostatic everywhere provided that the outer layer is of uniform thickness. The earth is, however, in rotation, but this only means that the shells of uniform density instead of being spheres must be the equipotential surfaces for the combined gravitational and centrifugal force fields. It is simpler to consider the stationary sphere, as it makes no serious difference to the argument.

It has been shown that the condition for hydrostatic pressure only to be present in the earth is that the density is a function of the depth only. Now the density of matter depends on its temperature and state. Thus if a medium at a given temperature is capable of existing in two states one of which is strong, i.e., solid, and the other weak, i.e., a highly viscous liquid, we would expect, arguing from the normal behaviour of solid and liquid phases, that the weak phase would be less dense that the strong. This condition is tacitly assumed in applying the theory of the change of freezing point with pressure to the question of the thermal stability of the earth's crust at all. If, then, at some depth in the earth a temperature is reached at which the medium loses its strength, the condition for the stresses in the outer crust to be purely hydrostatic is that the surface of change is an equipotential surface. For a stationary sphere the equipotential surfaces are concentric spheres.

We are probably justified in assuming that the change of state will take place at some fairly definite temperature. We may neglect for the moment the change of melting point with pressure as this is only a small effect. The conclusion we are led to is that if a convective layer exists in the earth, and if the presence of this layer is to introduce no shearing stresses in the outer solid shell, the surface of the layer and consequently the melting point, i.e., change of state, geotherm must be an equipotential surface.

It seems impossible for the earth to satisfy this condition owing to the presence of the continents. It would seem hard to deny that the temperature at a given depth from the geoid must be greater beneath a continent than beneath the ocean, owing both to the greater thickness of the continent, which increases its thermal insulation properties, and also to the much higher radioactive content of the continental rocks. Thus the existence of a convective layer must introduce shearing stresses in the upper crust, and with it the possibility of the mechanical failure of this crust, if the change point geotherm departs too far from the equipotential surface.

Fig. 5 shows the condition of affairs that is probably present in the earth due to the presence of the continental blocks. As an approximation the curvature of the earth is omitted. Let ρ_1, ρ_2, ρ_3 be densities of convective phase, strong phase, and continent respectively; h_1, h_2, etc., the thicknesses of the various layers measured from the equipotential surface drawn through the lowest point of the change point geotherm. Call P_0 the pressure at this depth, which must be the same everywhere, since below this level the pressure is purely hydrostatic, as the convective layer has no strength. The condition of equality of mass in the crust is satisfied if $\rho_1 h_1 + \rho_2 h_2 + \rho_3 h_3 = \rho_2 h_4$. Consider, however, the state of affairs at a point C. The vertical pressure $= P_0 - \rho_2 h_1 g$,

but the horizontal pressure will be equal to the hydrostatic pressure in the convective layer which is $P_0 - \rho_1 h_1 g$. Therefore at C the horizontal stress exceeds the vertical stress by an amount $(\rho_2 - \rho_1)h_1 g$, i.e., the material in the portion of the solid crust below C is subjected to a vertical tension superimposed on a large hydrostatic pressure. If ρ_2 is less than ρ_1 this portion will be subjected to a vertical compression (plus a similar hydrostatic pressure), the only case in which the stresses are purely hydrostatic being when $\rho_1 = \rho_2$.

The problem of the stability of the portion in question is very similar to that of a compensated mountain range already considered by Jeffreys (9). He concludes that the strength implied by a compensated mountain system is equal to the load. If we apply this result to the problem in hand, we see that $(\rho_2 - \rho_1)h_1 g$ cannot exceed the tensile strength of the crust under the appropriate hydrostatic pressure when $\rho_2 > \rho_1$, or that $(\rho_1 - \rho_2)h_1 g$ cannot exceed the compressional strength of the crust when $\rho_2 < \rho_1$. In either case a limit is placed to the possible departure of the surface of the convective layer from the equipotential surface, just as the strength of the crust places a limit on the possible departure of the surface of the globe from the equipotential surface.

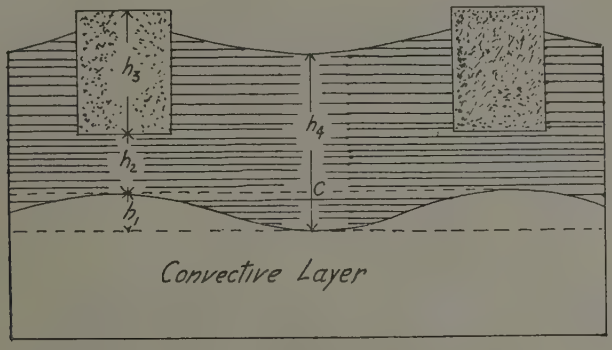

FIG. 5.

It is difficult to arrive at any definite figures as to the maximum value of h_1 owing to our ignorance of the strength of the crust and of the value of $\rho_2 - \rho_1$. If we take the case of a heavy crust resting on a lighter convective layer, as would happen if both were composed of the same materials, the tensile strength of the crust is the ruling factor. The tensile strength of the igneous surface rocks is about 50 kg. cm.$^{-2}$ at zero pressure (10). The effect of pressure on tensile strength has apparently not been investigated. Suppose, however, that we assume that it increases it, so that we might take the tensile strength of the crust to be 100 kg. cm.$^{-2}$. The density of the crustal materials is about 3 g. per c.c., and ordinary basalt on melting at air pressure changes in volume

by about 10 per cent. Thus near the surface if the basalt actually melted $\rho_2 - \rho_1$ would equal 0·3 g. cm.$^{-3}$, which only allows a maximum departure of the surface of the convective layer from the equipotential of 3·3 km. If this value is exceeded the thicker crust under the oceans would give under the strain, presumably by the lower layers breaking off and sinking in the lower lighter substratum. It is true that this phenomenon would explain how the heat which tends to accumulate under the continents might be got rid of without assuming any shift of the outer crust relative to the inner layers, but the catastrophic nature of the proceeding seems to be rather too great to agree with the more gradual changes observed in earth history.

We can, of course, increase the allowable departure from the equipotential by assuming that $\rho_2 - \rho_1$ is less at high pressures. This is probably true, due to the greater compressibility of the liquid phase. Thus if $\rho_2 - \rho_1$ was only 0·03 g. cm.$^{-3}$ the maximum departure might be 33 km., but the breaking of the outer crust would be even more catastrophic if it did occur.

On the grounds of the general stability of the crust, it would, accordingly, seem more reasonable to assume that the crust and the convective layer, if any, are not of the same material but that the convective layer is of greater density than the crust. This agrees with what we would expect from the effect of gravitational separation. In this case the compressional strength of the crust will govern the allowable irregularity of the surface of the convective layer, and as rocks are much stronger in compression, a correspondingly greater departure from the equipotential surface would be possible. Furthermore, the yield of the upper crust if it did occur would only result in increasing the uniformity of thickness of the crust, and there would be no foundering of portions of the crust.

I should like to point out that in the above argument the effect of the viscosity of the convective layer has been neglected. This seems justifiable if the convection currents in the layer are not of a cross-section comparable with the size of the earth. Holmes' convection current theory, however, assumes that such is not the case, and the possible effect of these on the stresses in the outer crust requires further investigation. As such large convection currents imply also widespread differences of density in the convective layer their effect on the gravitational field must also be considered. As far as I know this has not yet been done.

There is one criticism of Holmes' theory which I should like to make. He objects to Joly's theory on the grounds that it leads to long periods of tension in the outer crust, followed by comparatively short, much more intense, periods of compression. On these grounds he prefers the convection theory which allows for the possibility of simultaneous compression and tension. There is one point which he seems to have neglected. The main difficulty with the contracting earth theory is with the total quantity and the distribution of the radioactive elements present in the earth. In formulating any alternative theory we may deny either one or both the requirements of the contraction

theory. If we imagine that the distribution is not that required, we will have a slowly cooling earth in which convection currents may still persist at not very great depths. If, however, we assume that the total amount of the radioactive elements is greater than that demanded, the earth as a whole at present must be accumulating heat in its inner layers. This will lead to expansion either due to change of state or to increase of volume with temperature, and hence to a state of tension in the outer crust. The convection currents might possibly slightly modify the distribution of this tension in the outer crust but they cannot destroy it. Any theory which is built on the assumption that the amount of thermal energy in the earth fluctuates about a steady mean value, must involve that, on the whole, the crust is in tension when the thermal energy is increasing and in compression when it is decreasing. The magnitude of the tension and compression will depend on the amplitude of the fluctuation, and thus as Holmes' theory would seem to envisage much smaller changes in the total thermal energy than Joly's theory, it would lead to a smaller amplitude and higher frequency in the change of stress in the crust, if in both theories the total amount of radioactive elements is taken as the same. Periods of mainly tensional stress must, however, occur.

We may summarize the views advanced in this paper as follows:—

1. The condition for the existence of a permanent convective layer in the earth is that below a certain depth the adiabatic gradient is greater than the freezing point gradient.

2. The distribution of radioactivity in the original crust of the earth could not have been that required by the cooling earth theory, and consequently remelting of the original crust must have occurred.

3. The present distribution of radioactivity is most easily explained on some theory which allows for refusion of the crustal materials.

4. The presence of a permanent convective layer in the earth at moderate depths will introduce shearing stresses in the crust, and the nature of the stress renders it likely that the convective layer if it exists must be denser than the overlying crust.

5. Holmes' Convection Theory, while it may diminish world-wide tension in the crust, cannot entirely eliminate it during the periods in which the thermal energy of the earth is increasing.

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Trinity College, Dublin,

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No. 3.

ABNORMAL CONES OF *FITZROYA* AND THEIR BEARING ON THE NATURE OF THE CONIFER STROBILUS.

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(Assistant in the Department).

(Plate 1.)

[Read December 19, 1933. Published separately February 1, 1934.]

The genus *Fitzroya* includes one species, *F patagonica* J. D. Hooker [*F. cupressoides* (Molina) Johnston]. A native of Chili and Nth. Patagonia, it is fairly hardy, and is represented in many Conifer collections in these islands. Practically all the trees, however, are ovulate only, but there is one well-known specimen in the gardens at Hewell Grange, Worcestershire, which commonly carries staminate cones also. It has also been long on record that the Hewell Grange tree produces with fair frequency hermaphrodite cones. In the course of working through the life-history of *Fitzroya,* a number of such cones were obtained, and, in addition, many abnormal staminate cones were received, which are perhaps of even greater interest. It is proposed here to describe these abnormalities, and to suggest the possible bearing they may have on our conception of the nature of the cone structures in both the staminate and ovulate strobili.

We wish very sincerely to acknowledge the kindness of Mr. F. Molyneux, head-gardener of Hewell Grange, who forwarded regular supplies of coning *Fitzroya.*

Abnormal Staminate Cones.

Reference has already been made, in a previous communication on the development of *Fitzroya* (2), to the normal cone.

The abnormal cones are shorter and rather spherical, although, as is to be expected in such cases, numerous intermediates occur. The shorter length is mainly due to a lesser number of stamens being present, the cone axis stopping rather abruptly and in a manner rather similar to that shown by the ovulate

cone. At the base of the cone the first fertile stamens are usually normal. The adaxial appearance is shown in Pl. **1**, 1. The roundish to oval pollen-sacs are attached to the filament where it is expanding out to form the lamina, and are limited in number and in position. Higher up in the cones the pollen-sacs on each stamen may become more numerous, developing towards the upper side of the stamen, which may eventually carry a complete circle of them round the distal end of the filament. The normal pollen-sac is carried on a short stalk (Text-fig. *A*). In these abnormal cones the stalk of a pollen-sac may be much elongated, and may arise in a more proximal position, even from practically the base of the filament. In this change more than one pollen-sac may be involved, a stalk being formed carrying up to three sacs. Each of these sacs is attached to this separated stalk or pedicel by its own short basal stalk, just as the normal sac is to the filament, the whole giving the impression of some peculiar form of small "branching stamen." The adaxial view is shown in Pl. 1, 2. In some cases the lamina gradually disappears, an intermediate stage with a very small reduced lamina being shown in Pl. **1**, 3 and 4. In the specimen drawn the cone apex gradually narrowed in a rather normal manner. In the normal cone the stamens are ordinarily in whorls of three, but the top whorl seldom has three, and may carry only one almost terminal stamen. This condition appears in these figures with the last stamen lacking the lamina. The scars of detachment are those of other stamens and of separated groups of branching stalks carrying pollen-sacs. In cones showing this tendency reduction in the number of pollen-sacs commonly accompanies reduction of the lamina. A more interesting type shows a further change. In these cases the apex of the cone is flat, and recalls the apex of the ovulate cone. It may be occupied by a number of the "branching stamens" to which attention has been called, these being situated well in on the cone axis, where the bases of the in-running filaments have lost their separate and distinct nature. In some cases the isolated "branching stamens" can be related to what should apparently be their filaments; thus, in Pl. **1**, 2, if the lamina were less developed, and the branching group more distinct and well down on the filament, the group would occupy a position more or less on the top of the cone axis but still readily related to its proper stamen. Often, however, no such clear relation can be established on visual examination. Pl. **1**, 5, shows this condition. The surrounding stamens are removed, leaving only those branching groups not readily breaking away when the rest of the stamens were detached. Almost any imaginable intermediate stages between those drawn may be met with.

We are in complete agreement with the view that abnormalities must be interpreted with extreme caution, if, indeed, we can use them at all as evidence in any morphological argument. It is obvious that we know little of the laws governing normal development. Why, considering two neighbouring buds, for example, does the one develop vegetatively, the other into a staminate or ovulate cone? How then can we proceed to interpret the abnormal, knowing nothing of the morphological or physiological instability which underlies its appearance?

And, if the staminal modifications of *Fitzroya* stood alone, they could well be passed over as an interesting record, and there left. But when they support a bulk of evidence all pointing in one direction, they then become suggestive and require further consideration.

The question on which they bear is our conception of the Conifer stamen. On a cursory glance this structure seems to be simply an ordinary leaf, fertile and carrying sporangia below. But another view may be taken. When presenting some evidence from *Larix* in possible support of this view the data were summarized (1). The argument is briefly this—detailed references need not be repeated here, and many of the facts are well known. The stamen of *Taxus* is peltate, carrying a number of pollen-sacs symmetrically and distally. *Torreya* shows a reduction in the number of sacs, the upper being replaced by resin sacs, although fully peltate stamens may sometimes be seen. In the developing stamen of *Ginkgo* the young stages are peculiarly symmetrical, with resin areas above the filament and young sacs below—strikingly similar to the condition shown at this stage by *Torreya*. The two sacs, as is well known, later hang down from a most un-leaflike filament. The inference can be drawn that the stamen of *Ginkgo* is reduced from an earlier type with a larger number of distal sporangia, an inference supported, perhaps, by such fossils as *Stachytaxus*. In both of the living phyla mentioned the axis of the cone lifts itself up from the covering basal bracts and is bare of any leaflike growth on its lower part, there being normally no grade between the stamens and the basal leaflike structures. A similar condition is very striking in the Abietineae —*Tsuga* and *Pseudolarix* being quite remarkable. In these two genera the staminiferous part of the cone is carried up on an extreme elongation of the lower part of the axis like the stipe of an Agaric. In genera of other groups—*Sequoia*, *Athrotaxis*, etc.—a similar phenomenon can be seen. In some of these there is undoubtedly developed a flattened and somewhat leaflike expansion of the distal part of the stamen, but, in *Larix* and *Pseudotsuga*, for example, such an expansion is not a lamina but rather a rounded knob, somewhat like that in *Ginkgo*, and possessing two resin-sacs. In the young stages these sacs are symmetrically placed and similar to the sporangia. Vertical sections at this stage of *Larix* are in close agreement with those of *Torreya* and *Ginkgo*.

The tentative conclusion can be drawn that the Conifer stamen is not a fertile leaf in the sense that it ever passed through a flattened photosynthetic stage in its phylogeny, but is rather of a sporangiophoric nature, being primitively a specialized reproductive branch carrying sporangia distally. The development of a lamina or leaflike expansion, with limitation of the sporangia to an abaxial position, and in number, is, on this view, associated with biological requirements, of which the need for protection is possibly one.

Pilger, in a recent article, has commented on this (6). Such a view, he maintains, can only be derived from a consideration of those forms in which there is a wide separation between stamens and foliage leaves, but the argument, he claims, breaks down when such a group as the Cupressineae is examined.

Here, he says, there is no such separation of foliage leaves and stamens, but, the cone being usually carried terminally on small branches, the leaves pass directly into the stamens, which are true sporophylls. In the first place, even as a claim of fact this statement cannot pass unchallenged. In the Cupressinean forms available the staminate cone, as soon as growth begins, is carried up on a distinct terminal stalk in a manner exactly comparable to, though not quite so marked as, that in *Tsuga, Taxus* or *Larix*. There is, thus, a very clear separation at maturity between the reproductive and vegetative areas; in many cases, even in the bud, the staminate cone is neatly delimited, if only by colour and appearance, from the true leaves with which it comes basally in contact. In *Fitzroya* also this condition is clearly seen. But, apart from this consideration, the interest of the abnormalities in the staminate cone of the genus is sufficiently obvious. *Fitzroya* shows the development of a stamen with radially arranged distal sporangia; this structure can apparently branch and carry the sporangia terminally on these branches. We see, therefore, in a representative of a group whose normal structure, according to Pilger, is in direct opposition to the interpretation of the stamen outlined above, the development of a condition strongly in support of it. When we thus find in so many different Gymnosperm groups the same apparent tendency, it seems possible that these abnormalities in *Fitzroya* may, indeed, be of the nature of reversions. When, in *Cordaianthus*, in living and possibly fossil Ginkgoales, in the Taxads, in the Abietineae, and now in the Cupressineae, we find evidence in favour of the interpretation of the Conifer stamen, not as a sporophyll, but as some form of special reproductive branch, it is not entirely unreasonable to suggest that this conception of the stamen is at least worthy of consideration.

If this view is accepted certain implications would naturally follow. It could not be contended that the primitive stamen of the phylum from which the Conifers and Ginkgoales arose was a simply peltate one like that of *Taxus*; that type is specialized along one line of protection of spores in a cone. But even a cursory examination of the fossil record of early Devonian times shows clearly the widespread occurrence in plants of that period of two structural characters—the lack of the flattened photosynthetic lamina which we call the leaf, and the carriage of sporangia terminally on the final ramifications of a more or less highly branched system. The drawing of an early Devonian landscape in Seward's recent book (9) and an article by Kräusel (4) are interesting in this connection. It is possible to consider that the pollen sporangia were originally carried terminally on the ends of a branching system which became reduced in the course of time to a single simple structure carrying the sporangia distally. The present forms of the various stamens may be developments from this, associated with biological needs. The branching structure may have already become specialized even before the photosynthetic flattening was impressed on other members of the branching system of the plant to give the leaf. If this view of the leaf be accepted, that it arose as a photosynthetic specialization of a large or small branching system, the foliage leaf

and the stamen are essentially homologous in the sense that they are both specializations of structures primitively essentially similar, one given over to reproduction, the other to nutrition; but, in the Conifer stamen, these two functions never overlapped. To anyone who considers the plant, not as a rigid morphological entity, but as a living plastic thing in which the ontogeny of, say, the leaf, is determined by a complex of physiological interactions of which we know very little, there is nothing remarkable in the slight resemblance in some cases between the more or less distal laminated expansion of the stamen and neighbouring foliage leaves. It is just as remarkable to find them so frequently distinct.

Abnormal Ovulate Cones.

The normal ovulate cone of *Fitzroya* has been frequently described, and recently Sahni (7) has added to our knowledge of it; but, while the occurrence of hermaphrodite cones on the tree at Hewell Grange has long been known, no full account of their structure is available.

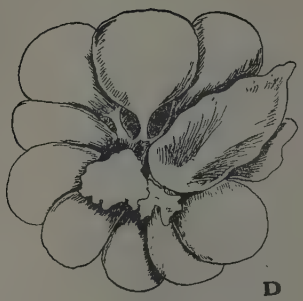
The base of the cone presented in most cases a varying number of whorls of more or less normal stamens. The uppermost whorl before dissection sometimes showed a fairly normal appearance—the three broad pedicels joining to form a sort of terminal platform, on which clustered a number of ovules more or less normally related to the pedicels, and surrounding the central columella of three elongated and diverging resin sacs so characteristic of *Fitzroya*. In practically all cases, however, this upper whorl carried pollen sacs below. Pl. 1, 6, shows one such member of the cone with the abaxial pollen sacs and one adaxial ovule—the other overlapping ovules having been removed for clarity in the drawing. This structure obviously resembles the peltate form of stamen which occurred so frequently in the abnormal staminate cones, the upper pollen-sacs being here replaced by ovules. The number of the ovules was commonly sufficient to complete with the pollen-sacs a ring of sporangial structures encircling the pedicel distally. In a big majority of the cones examined a number of intermediate structures between ovules and pollen-sacs appeared, the development of perfect ovules being, in many cases, suppressed. Numerous grades existed between structures similar to the complete peltate stamen, in which the adaxial completion of the sporangial group was composed of normal pollen-sacs and those in which it was composed of ovules. The naked eye appearance, as seen on looking down on the top of the cone, varied accordingly.

Some of these sporangial intermediates are shown in the Text-fig. *B–K*. *B* is one of the branching structures carrying two pollen-sacs, one, however, much smaller than the other. In *C* one of the sporangia in a similar structure is replaced by a flap of tissue. *D* is the adaxial view of a complete structure from an abnormal ovulate cone, showing *in situ* the branching sporangial stalks and a flap of tissue like *C*. A more elaborate condition of *C* is outlined in *E*.

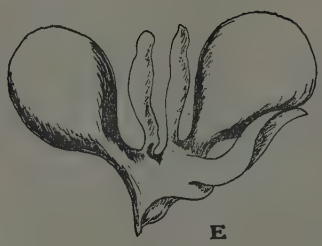
A

B

C



D



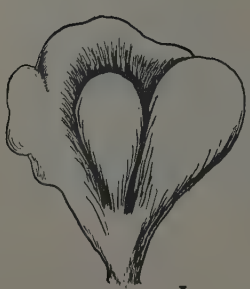
E

F

G

H

I



J

L

K

In *F* one flap is larger and more regular, surrounding one sporangium; one pollen-sac is still distinct while another structure, partly flap and partly sporangium above, is also seen. *F*, *G*, and *H* are more regular variants of the same. In *I* the large integument-like flap surrounding the central structure, which resembles a nucellus, is still open to one side, and is still joined with a more regular sporangial body. Such a body is still distinct in *J*; in *K* it is still visible on the right-hand edge, but forms only a small swelling of the flap. This flap, still open along one side, is now extremely integument-like, expanding along one side to form a small wing, and contracting towards the top in a manner suggestive of the micropyle. These latter forms grade rapidly into typical ovules. Only a selection of the many intermediate stages linking up ovules and pollen-sacs have been drawn. The columella becomes included commonly in these changes. Just as the branching stalks may occupy the centre of the axis in the abnormal staminate cone, these abnormal ovule-pollen intermediates may encroach on the area on which normally the columella is situated. Any or all of the columella branches may be affected, losing their identity, and becoming indistinguishable from some of the nucellar and other sporangial structures. The morphological nature of the columella is not very clear in many Conifers in which such a structure occurs. In *Thuja*, for example, it seems to be the ultimate pair of sterile scales, but in *Fitzroya* these abnormal cones strongly suggest that it is essentially a group of unintegumented sporangia.

These ovule-pollen abnormalities may mean little or nothing, but, apart from the columella question, they are open to an obvious—perhaps a too obvious—interpretation. They strongly suggest that the integument of the gymnosperm ovule is a multiple structure derived from the sterilization and fusion of neighbouring sporangia. This is essentially the thesis elaborated by Miss Benson on quite different grounds; and we have, perhaps, here definite material evidence in favour of her view. In this connection, however, it seems advisable to consider if it is in any way necessary strictly to homologize certain parts of, say, *Heterotheca* and *Lagenostoma*, as Miss Benson seems to find it incumbent. Both have become specialized along distinct lines—one along the line of seed development, the other along that of free spore formation. The original homosporous structures from which both arose may well have been of a more primitive and more generalized type.

These abnormal cones of *Fitzroya* have a further interest. If we accept, temporarily, the idea of the nature of the stamen already outlined, certain conclusions seem naturally and necessarily to follow when we consider the organization in general of the ovulate strobilus of the Conifers. As is well known, one view, which excludes perhaps *Taxus* and *Torreya*, considers the cone as formed of sporophylls carrying ovules on the adaxial surface, the later swellings and other changes being interpreted as placental outgrowths, ovular extensions and the like. The so-called bract is thus a simple sporophyll, and is homologous with the stamen. But one difficulty which this interpretation presents is the occurrence of the ovules on the adaxial and the pollen-sacs on

the abaxial surface of the sporophyll. What was the primitive position? If ovules and pollen-sacs are homologous sporangia they were carried, presumably, in similar situations in their ancestral homosporous stage. This difficulty has hardly been adequately faced, and Thomson's suggestion (10) that the ovules have been secondarily displaced to the adaxial side in phylogeny needs further evidence. Apart from this, the view has been widely accepted.

The hermaphrodite cones of *Fitzroya* certainly support the claim that the stamen and the bract are essentially similar structures. In fact the occurrence of the variations already described almost amounts to a proof. If, then, the stamen is not considered a sporophyll in the sense of anything like a vegetative leaf carrying sporangia, neither can the bract be so considered; if the stamen is considered to be derived from a primitive reproductive branching system carrying sporangia, possibly terminally on the ultimate ramifications, then the bract can be considered of a similar nature. The tendency in complete reduction to carry sporangia abaxially on the stamen, which seems perhaps to facilitate pollen liberation combined with protection in the young stage, can be contrasted with the tendency to limit the ovules to the adaxial side to facilitate pollination. By thus not considering the bract or stamen as a leaflike sporophyll the difficulty referred to, of accounting for the different positions on a similar structure of homologous organs, disappears. Ovules may occasionally develop abaxially in *Fitzroya*, displacing pollen-sacs in the abnormal scales. Text-fig. *L* shows such a case. The ovule is not quite normal, the micropyle, too flaring, exposing the projecting nucellus. The drawing, of course, is of the appearance as seen on the outside, the ovule being really attached to the filament, and directed downwards and outwards.

This phenomenon is paralleled in *Saxegothaea* (10). It is also of interest in this connection, that in *Sequoia, Athrotaxis,* and others, the ovules, while still quite young, are carried well out on the bract, which at an early stage actually develops a very distinct stalk. At the youngest stages so far available no indication of an axillary structure is shown. Except that the ovules are above and the pollen sacs below they are carried in essentially the same position on their corresponding bracts. The well-known abnormality in *Ginkgo,* where many ovules are carried each terminally on a portion of a branching system, may possibly indicate the type of system from which we consider bract and stamen to be reduced. It is further of great interest that Schoute (8) has shown on the basis of phyllotaxy that the ovular structure in *Cordaianthus* replaces a bract, and that there is thus no axillary relationship between them. It is not clear whether the same relation holds for the staminate cone, but, in any case, an interesting parallelism arises. The cone of *Cordaianthus,* like that of the Conifers, may be considered as a regularly arranged group of reproductive branches; in *Cordaianthus* the function of protection has been effected by the sterilization of some of the structures, in the Conifers by the development of the distal end of the structures (and by secondary growths and swellings) while all remained fertile.

Such a conception of the bract could be applied without strain to the Cupressineae, Callitrineae, Sequoiineae, and Araucarineae. Its application to the Abietineae is not so obvious, even though it seems eminently reasonable to accept that they and the general Cupressinean complex are monophyletic. However, in the less modified hermaphrodite cones which occur with some frequency in *Picea, Larix,* and related genera, the ovuliferous scale may be associated with a stamen and not with a bract. The homology between stamen and bract is here again suggested, and the old concept that the scale is a placental or ovular outgrowth brings this group into line with the others. But there is a strong claim that the ovuliferous scale of the Abietineae is a primitively axillary structure. Leaving out of account the possible interpretation of abnormalities, the development of the scale, as described, for example, by Goebel in *Pinus montana,* seems to indicate that the scale is axillary. If, however, in the Cupressinean complex the ovules are carried on the bract, and may be replaced by pollen-sacs, and if any close parallelisms in structure are sought for between this group and the Abietineae, in which the ovules, although bract and stamen are still homologous, seem to be carried, not on the bract, but on an axillary structure, then an obvious dilemma is presented.

Now, among the last of Goebel's (3) contributions to organography is a completion of a scheme of construction of the Conifer strobilus, a scheme which in many ways is simple and comprehensive. He rejects the idea of an axillary branch in the cone, in the sense in which branch is used in everyday description, but retains the axillary concept. The unit of the cone is the bract carrying a number of axillary sporophylls, each with a terminal ovule. The primitive nature of the sporophyll is not indicated; it is supposed now to be reduced to a vestigial structure, a "Sporophyllreste," practically an ovular stalk. In the Abietineae two such structures arise in the axil of the bract, fused from the embryonic state. This is the axillary structure which is seen in development. An ovule arises terminally on each, subsequently becoming secondarily inverted, and from each "Sporophyllreste" an outgrowth arises. These also are early fused, and give the scale. This primary conception runs through the whole scheme. In *Cryptomeria,* and probably in *Cunninghamia,* the outgrowths from each "Sporophyllreste" are distinct in the early stages. In *Cryptomeria* the "Sporophyllreste" are much reduced, but the divided outgrowth arises distinctly later than the ovule, and between it and the bract, indicating to Goebel that it is an outgrowth, and not a reduced axillary branch carrying ovules. Basal growth of the bract and the outgrowth produces the adult scale. The abnormal cone of *Pinus maritima* (?) illustrated in Goebel's Fig. 1859 actually shows a bract carrying three separate ovules, each provided with a separate scale-like expansion. In the Cupressineae the outgrowth of the "Sporophyllreste" is no longer connected in development with the axillary ovule, but has become secondarily displaced on the bract. Goebel's Figs. 1855, 1856, 1864, 1869 illustrate these and other points. The scheme is extended in a very simple manner to cover the whole gamut of the Coniferales and the

Ginkgoales, the interpretation of the Taxad structure being particularly attractive. The occurrence, recorded by Mitra (5), on Araucarian cone-scales, of two ovules each with its own ligule, is of obvious interest in this connection.

A full discussion here of Goebel's scheme is not proposed, but brief reference to certain points is necessary. His refusal, even in the face of all the well-known abnormalities, to accept the idea of an axillary branch in the Conifer strobilus is important. He suggests that the organization may date from a time when leaf and axis were less sharply differentiated than they are at present. This is the crux of the position, and the view which this paper is intended to emphasize. The idea that the ovuliferous scale of the Abietineae is a reduced form of axillary leafy branch carrying sporangia on the leaves is an endeavour to interpret the reproductive structures of the Conifers in terms of their present vegetative condition. But the Conifers are a group of very ancient lineage. It is eminently probable that the main plan of the archaic cone was achieved early, and either before or independent of the vegetative and photosynthetic organization; the cone must be interpreted in terms of some such archaic plan, and not with reference to present-day vegetative form. At what stage in the phylogeny of the primitive Conifer alliance did differentiation take place between vegetative and reproductive areas? At what period and in what manner, even in the vegetative body, did a structure, originally, in all probability, of a more or less dichotomously branching nature, develop the characteristic of bearing branches in the axils of specialized leaves? Was such a stage ever impressed on the reproductive parts or in what exact manner? These are the questions that matter in the interpretation of the cone.

Goebel's idea of axillary sporophylls seems strained; and it is here perhaps that the abnormal ovulate cones of *Fitzroya* may ease interpretation. In *Fitzroya* the bract and stamen seem strictly homologous, the ovules and pollen-sacs replacing each other in the same position on the same structure. It has been further suggested that both stamen and bract are reduced from some form of sporangium-bearing branching system. In the normal stamen and the bract of the Cupressinean complex this system is reduced to a simple structure, the terminal part expanded for protection. In the abnormal male cone some of the stamens show the pollen-sacs carried on simple or branched stalks. If the primitive branching system carrying the ovules was reduced in a similar manner, and the ovules limited in number on such a reduced branching stalk in an *adaxial* position, the rest of the system developing as in the stamen into the protective bract, then the Abietinean system is readily attained. The scale can be an outgrowth of the placenta or ovular base, a condition actually reproduced in the abnormal sporangial stages of the Text-figure. The ease with which such scale-like structures are produced seems strongly to support the idea of the scale as just such an outgrowth. Again, just as in the abnormal stamen the branching groups may be proximally attached to the filament or even apparently attached to the axis, so the axillary position of the developing Abietinean scale may be only apparent. The complete structure, bract *and*

scale, would be homologous with a single stamen or a single ovule-bearing bract of the Cupressinean complex. A consideration of the relative positions of the male and female cones in practically every genus except *Pinus* points also to a very complete homology between the parts, an homology readily followed from this point of view. This modification frees Goebel's scheme from two weaknesses—the concept of axillary sporophylls and the separation of "Sporophyllreste" outgrowth and ovule in forms like *Cupressus*. Here the swelling on the bract may be simply what it appears to be—a swelling, a specialized growth in relation to cone maturity and seed protection. The axillary nature of the theoretical sporophylls does not seem really necessary to Goebel's broad scheme. This conception can be removed from the scheme without in any way affecting the other homologies which he follows, and with which in the main we are in agreement.

The suggestions here outlined are put forward in a purely tentative manner, and for that reason no endeavour is made at present to analyse them more fully. They are put forward solely because they seem to arise naturally and necessarily from a consideration of the abnormal cones of *Fitzroya*. The examination of these cones has necessitated a rather complete modification of views outlined, again very tentatively, in an earlier communication (1). But, whatever final view is adopted in the future of strobilus organization in the Conifers, one point is definitely claimed here. The primitive organization cannot be got at by visualizing the cone as developed from a vegetative branch carrying sporangia in not too definite a manner. Comparisons with Ferns or Cycads or Pteridosperms are of little value. The roots of the Conifer phylum are deep and separate, as far back as we know them, from the other seed-plants. Their cone structure is, then, probably a very ancient feature, and we must seek its origin in the reduction of the primitive non-laminated reproductive branching systems of the early Devonian or pre-Devonian plants. Among the plants which succeeded in elaborating a seed from their homosporous ancestors two lines of development appear. In one, parts of the primitive branching system became specialized and photosynthetic to form the leaf, but carrying in the change the sporangia, thus giving the Pteridosperm type of structure; in the other, the leaf development and function never overlapped the reproductive function, the primitive reproductive branches became condensed and reduced to give us the cones as we know them from *Voltzia* and *Cordaianthus* to *Pinus* and *Cupressus*.

A final word seems necessary in connection with Prof. Walton's recent discovery of a bract-scale in the cone of *Voltzia Liebeana* (11). This record is of great interest, showing as it does that the Abietinean plan of cone structure is very old. Prof. Walton, however, goes on to say: "The scale of *Voltzia Liebeana* appears to consist of a group of leaf-like structures, . . ., the whole structure probably representing a reduced axillary branch in the axil of the bract-scale with which it is partially fused at the base." Such a statement does not seem justified on the evidence. Flatness of a structure is no criterion

of a leaflike nature, and no more proof of the axillary branch nature of the scale is afforded by *Voltzia* than by *Pinus* or *Cryptomeria*. Ovules carried directly on the bract, as in *Fitzroya*, with placental outgrowths or outgrowths of an ovular stalk or base with early fusion and subsequent basal intercalary extension, could just as readily give the *Voltzia* condition. Prof. Walton is also of the opinion that the divided (and, therefore, more complex?) nature of the scale does not favour the view of a placental outgrowth; in so primitive a representative a much simpler structure is to be expected. Without considering the subtleties underlying the distinction between placental and ovular outgrowths, actually on Goebel's view of the scale as an outgrowth of the "Sporophyllreste" (or, as we consider it, of placenta, ovule stalk, or ovule base), the primitive condition would be that of separate outgrowths for each ovule—that is, a divided scale, as in *Voltzia* or *Cryptomeria*.

Summary.

1. The structure of abnormal staminate and hermaphrodite cones of *Fitzroya* is described.

2. On the basis of these structures it is tentatively argued that:—

(*a*) The stamen and the bract of the ovulate cone are homologous.

(*b*) There is no axillary structure, particularly no reduced branch, in the organization of the ovulate cone, the ovules being directly related to the bract.

(*c*) Neither bract nor stamen is a sporophyll in the sense of a structure in any way similar to a vegetative leaf carrying sporangia.

(*d*) Both bract and stamen are the end development of an extreme reduction of a primitive reproductive branching system carrying sporangia, probably terminally, on the ramifications; the main plan of the cone being attained before, or at least independently of, the photosynthetic development which gave rise to the leaf.

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EXPLANATION OF PLATE 1.

(Drawn by Miss M. O'Leary. All × 30 approx.)

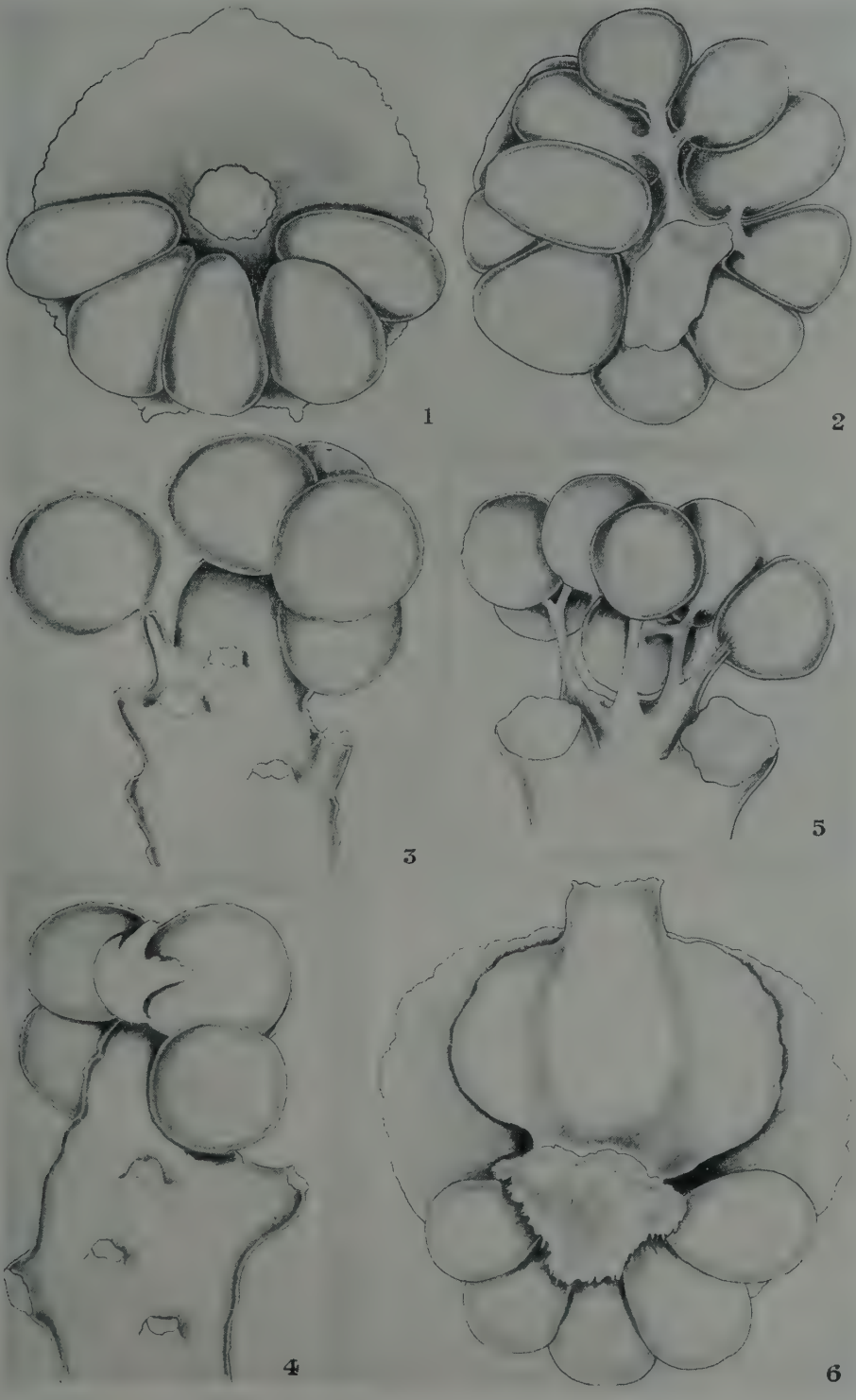
Fig. 1. Adaxial view of normal stamen.

Fig. 2. Adaxial view of abnormal stamen showing supernumerary pollen-sacs and the branching stalks.

Figs. 3 and 4. Two views of a stamen with reduced lamina. The scars of detachment are those of other filaments or of separated branching stalks like those in 2.

Fig. 5. Apex of cone occupied by the short branching systems carrying terminal pollen-sacs. The scars of the uppermost whorl of stamens are shown.

Fig. 6. Adaxial view of bract of hermaphrodite cone showing pollen-sacs below and one normal ovule above, the other ovules being removed.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No. 4.

A NOTE ON THE MOLECULAR COMPLEXITY OF AMYLOSE IN POTATO STARCH.

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The molecular complexity and colloidal state of starch render the investigation of this substance a difficult problem. The fact, however, that starch on hydrolysis yields a sugar, leads to the idea that intermediate products are formed in the stage of breaking down. In this respect the credit of the pioneer work belongs to C. O'Sullivan, an Irish chemist. He was the first to investigate thoroughly the action of malt diastase on potato starch at different temperatures. He showed the formation of eight dextrin products in the starch conversion, and found that the sugar product was maltose (1). Later (2) the relative proportions of maltose and dextrin formed at different temperatures were investigated. Crystalline dextrins were isolated by Schardinger (3) by inoculating a 5 per cent. starch paste with a potato culture of *Bacillus macerans*.

The starch molecule in these researches had been regarded as a homogeneous one, but Ling and Nanji (4) showed that the granule of potato starch consisted of two substances, the inner portion amylose, and the outer portion amylopectin. This discovery led to attempts to depolymerise these substances. Direct heating in solvents such as glycerol (5) yielded products which on cryoscopic determinations in water gave values agreeing with that of a di-hexosan from amylose and a tri-hexosan from amylopectin. Both of these substances may be obtained by acetylation of the starch components, and subsequent saponification of their acetates with alcoholic potash after heating with a small amount of a substance like benzene-sulphonic acid (6). The molecular weight of the acetyl derivative of amylose has also been determined directly by cryoscopic method in phenol by Bergmann (7), who found that tri-acetyl amylose gave a value agreeing with that of the acetyl derivative of a hexose anhydride.

Direct cryoscopic determinations of the molecular weight of amylose present great difficulty owing to its insolubility in most solvents. In previous work, however, with inulin (8) and glycogen (9) it was found that acetamide proved

a suitable solvent for direct determination of molecular weights. The values obtained indicate that the polysaccharides existed as comparatively small molecules in solution (10). Many interpretations of these results have been suggested, including the one that the low molecular weights may be due to polysaccharide water or alcohol complexes. The difficulty in removing the last traces of water or alcohol seemed to indicate that these substances were linked up with the solute in some constitutional form. In recent work (11) the behaviour of the polysaccharides in acetamide solution has been again subjected to further investigation. The substances were dried under different conditions, and the apparatus for determining the molecular weights was improved upon. It was shown that desiccation at 78° C. under 10 mm. pressure completely removed the water- and alcohol-content, and that the molecular weights in acetamide again corresponded to those of relatively simple molecules.

An interesting fact, however, emerged from the investigation, namely, that the polysaccharide always contained a slight amount of ash which in itself would not be capable of producing any appreciable depression of the freezing point of acetamide. Whatever forces are operative in the solution of the polysaccharide in the acetamide, it is definite that the cryoscopic results agree with the values corresponding to a small molecular unit.

The authors have now extended this work to amylose with interesting observations. In this connection it has been found that the molecular weight of tetra amylose in acetamide and in formamide gives values corresponding to *a* hexose anhydride (12). In the present work it was shown that the amylose dried at 78° C. at a pressure of 10 mm. for 30 min. gave the same percentage loss of weight as that dried at 137° C. in high vacuo for two hours. In the cryoscopic determinations in acetamide the amylose was completely dehydrated, and special precautions were taken to preclude the possibility of moisture entering during the addition of the polysaccharide to the solvent. Repeated determinations gave values agreeing with that of $C_6H_{10}O_5 \times 2$.

Whatever conflict of opinion there may be regarding the theoretical conclusions on these results, there can be no doubt as to the validity of the experimental observations. New facts have been disclosed by the behaviour of polysaccharides in acetamide solution, and some unexplained forces are being brought into play to yield such phenomenal conditions. The results, on the accepted principles underlying the determination of the molecular weight of a substance in a solvent by the lowering of freezing point, indicate the dispersion of the polysaccharide in solution to a small molecular state. The fact that a slight ash-content is present points to the view that it may be a vital factor in the depolymerisation or dissociation of the large aggregate molecule. What effect the acetamide has on the binding forces comprising this aggregate is a matter for interpretation, but the experimental results leave no doubt but that certain forces are brought into play in the solution of the polysaccharide in acetamide to reveal new phenomena.

Experimental.

A five per cent. solution of potato-starch paste was placed in a long thin glass vessel and immersed in a mixture of ice and salt at a temperature of – 12° C. for 12 hours. The fibrous mass obtained was then mixed with cold water, and the contents immersed in warm water until the starch fibres had "thawed." More water was added, and the temperature was maintained at about 40° C. After lixiviating with water at this temperature for about 4 hours, the contents were centrifuged, and the clear amylose solution filtered off. The residue was again treated with water at 40° C., centrifuged, and filtered. This process was repeated several times, and the filtrates were concentrated by evaporation under reduced pressure.

The solution was finally reduced in bulk by concentrating over a water bath. A scum or layer tended to form on top of the liquid similar to that formed in colloids, due probably to the denaturing of the aggregate. This layer on filtering gave long sticky fibres on addition of water, and remained insoluble even on boiling. Alcohol was added to the filtrate and the amylose precipitated. It was filtered off, washed with alcohol, and dried over calcium chloride in a vacuum desiccator. It was then exposed to the air for some time so as to get rid of most of the alcohol. When freshly prepared the amylose was soluble in cold water, but on keeping it became insoluble even in boiling water.

Drying Experiments with Amylose.

		Percentage Loss of Weight.
Amylose dried at 78° C. at 10 mm. over P_2O_5	for 30 min.	9·8%
„ „ „ „ „ „	1 hr.	9·9%
„ „ 137° C. „ „ „	30 min.	9·8%
„ „ 137° C. „ „ „	2 hr.	9·7%
„ „ 78° C. in high vacuo	1 hr.	9·9%
„ „ 137° C. „ „ „	2 hr.	9·8%

The amylose was found to be free from alcohol. It had an ash-content of 0·856 per cent., and further purification did not reduce the value.

Analysis of 4·670 mg. of substance gave 7·51 mg. CO_2.
2·54 „ H_2O.
0·04 „ Ash.

Corresponding to C, 44·24 per cent.; H, 6·09 per cent.;
calculated on ash-free substance.
$C_6H_{10}O_5$ requires C, 44·44 per cent.; H, 6·17 per cent.
Optical rotatory power determined in 5 per cent. NaOH—

$$(\alpha)_D^{20} = \frac{100 \times 0{\cdot}3}{1 \times 0{\cdot}2} = 150°.$$

The molecular weight of the amylose was then determined in acetamide at varying concentrations. The dehydration of the amylose was carried out under different conditions, and representative results of the different series of experiments are given. The acetamide was purified by crystallisation from chloroform. In the cryoscopic determinations in acetamide great care was taken to prevent the possibility of moisture entering during the introduction of the solute. The thermometer was fitted into the molecular weight tube, containing the solvent, by means of a ground glass joint. The temperature of the outer bath was maintained constant throughout the determination. The crystals of acetamide which crystallised in the determination of the freezing points of the solvent and solution were melted by electrically heating a small resistance wire fitted round the bottom of the tube. Constant stirring was maintained by the rise and fall of a platinum stirrer operated by means of an electro-magnetic device (13).

Molecular Weights of Amylose in Acetamide.

I.—Amylose dried for 1 hour over P_2O_5 at 78° C. and 10 mm. pressure.

	Acetamide.		0·72 % conc. of Amylose in Acetamide.
Bath Temp. . .	76°		76°
Interval between lowest and highest reading .	3 min.		3 min.
Reading . .	3·276°–3·280°		3·200°–3·206°
Mean . . .	3·278°		3·203°
Undercooling . .	2·5°–2·7°		1·8°–2·2°
Depression . .		0·075°	
Molecular Weight .		348	

II.—Amylose dried for 1 hour over P_2O_5 at 78° C. and 10 mm. pressure.

	Acetamide.		0·758 % conc. of Amylose in Acetamide.
Bath Temp. . .	76°		76°
Interval between lowest and highest reading .	3 min.		3–4 min.
Reading . .	3·252°–3·254°		3·176°–3·180°
Mean . . .	3·253°		3·178°
Undercooling . .	2·6°–2·8°		2·16°–2·32°
Depression . .		0·075°	
Molecular Weight .		367	

III.—Amylose dried for 2 hours over P_2O_5 at 78° C. and 10 mm. pressure.

	Acetamide.		0·88 % conc. of Amylose in Acetamide.
Bath Temp.	76°		76°
Interval between lowest and highest reading	2½–3 min.		3 min.
Reading	1·017°–1·021°		0·915°–0·918°
Mean	1·018°		0·916°
Undercooling	0·70°–0·78°		0·30°–0·40°
Depression		0·102°	
Molecular Weight		313	

IV.—Amylose dried for 30 min. over P_2O_5 at 137° C. in high vacuo.

	Acetamide.		0·758 % conc. of Amylose in Acetamide.
Bath Temp.	76°		76°
Interval between lowest and highest reading	3 min.		4 min.
Reading	3·270°–3·272°		3·188°–3·190°
Mean	3·271°		3·189°
Undercooling	2·5°–2·7°		1·9°–2·4°
Depression		0·082°	
Molecular Weight		335	

V.—Amylose dried for 1 hour over P_2O_5 at 137° C. in high vacuo.

	Acetamide.		0·689 % conc. of Amylose in Acetamide.
Bath Temp.	76°		76°
Interval between lowest and highest reading	4 min.		4–5 min.
Reading	3·278°–3·280°		3·208°–3·210°
Mean	3·279°		3·209°
Undercooling	2·7°–2·9°		2·5°–2·8°
Depression		0·07°	
Molecular Weight		357	

VI.—Amylose dried for 2 hours over P_2O_5 at 137° C. in high vacuo.

	Acetamide.		1·06% conc. of Amylose in Acetamide.
Bath Temp. . .	76°		76°
Interval between lowest and highest reading .	2–2½ min.		2½–3 min.
Reading . .	1·308°–1·312°		1·193°–1·197°
Mean . . .	1·310°		1·194°
Undercooling . .	0·54°–0·62°		0·50°–0·59°
Depression . .		0·116°	
Molecular Weight .		332	

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No. 5.

THE OXIDATION OF HYDRAZINE BY POTASSIUM FERRICYANIDE. PART I: THE INFLUENCE OF GASEOUS SUPERSATURATION ON THE MEASUREMENT OF REACTION VELOCITY. PART II: THE REACTION IN PRESENCE OF ACETONE.

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PART I: THE INFLUENCE OF GASEOUS SUPERSATURATION ON THE MEASUREMENT OF REACTION VELOCITY.

Many chemical reactions have been examined from the point of view of negative catalysis, but no investigation of this kind seems to have been applied to the oxidation of hydrazine. It seemed interesting, therefore, to see whether an inhibitor could be discovered for hydrazine oxidation.

The form in which nitrogen is liberated when hydrazine is oxidized depends on the oxidizing agent employed and on whether the medium is acid or alkaline. Some nitrogen gas is always set free, but in many cases hydrazoic acid and ammonia are formed, sometimes in considerable yield. This occurs, for example, in acid solution when the oxidizing agent is hydrogen peroxide (Browne, J. Amer. Chem. Soc., **27**, 551, 1905; Ber., **38**, 1925, 1905), ammonium metavanadate (Browne and Shetterly, J. Amer. Chem. Soc., **29**, 1305, 1907), potassium chlorate, bromate, iodate (Browne and Shetterly, ib., **30**, 53, 1908), persulphate, or permanganate (Browne and Shetterly, ib., **31**, 221, 1909). In alkaline solution hydrazoic acid is not usually produced in appreciable amounts, but ammonia may be, as when the oxidizing agents are hydrogen peroxide (Browne and Shetterly, ib., **31**, 221, 1909), copper sulphate, or Fehling's solution (Browne and Shetterly, ib., **31**, 783, 1909).

Some agents, however, such as mercuric oxide and chloride (Browne and Shetterly, ib., **31**, 783, 1909) and potassium ferricyanide appear to produce practically no ammonia or hydrazoic acid, and the comparatively straightforward nature of the reaction with potassium ferricyanide decided the writers to use the latter as oxidizing agent in the present work. The action of potassium ferricyanide has been investigated by Ray and Sen (Z. anorg. Chem., **76**, 380, 1912), who showed that in alkaline solution it oxidizes hydrazine quantitatively to nitrogen and water, and that the reaction can be used for estimating hydrazine by measuring the volume of nitrogen evolved. Cuy and Bray (J. Amer. Chem.

Soc., **46**, 1788, 1924) showed that hydrazine in alkaline solution is slowly oxidized by atmospheric oxygen, but that the attack of ferricyanide is so rapid that the error introduced by autoxidation under suitable experimental conditions is negligible.

The equation of the reaction,

$$N_2H_5HSO_4 + 4K_3Fe(CN)_6 + 5KOH = N_2 + 4K_4Fe(CN)_6 + 5H_2O + KHSO_4,$$

or

$$N_2H_5^+ + 4Fe(CN)_6^{---} + 5OH^- = N_2 + 4Fe(CN)_6^{----} + 5H_2O,$$

suggests a reaction of a high order, but it has been shown by Gilbert (Z. physik. Chem., **142**, 139, 1929) that the reaction in a solution buffered to p_H about 6 is of the first order with respect to each of three reactants, $N_2H_5^+$ ion, ferricyanide ion, and hydroxyl ion. It is therefore effectively second or third order, according as the hydroxyl ion concentration is or is not kept constant.

In a further paper (J. Phys. Chem., **35**, 3631, 1931) Gilbert examined the effect of light on the reaction. Illumination by two 200 watt nitrogen-filled Mazda lamps at a distance of 15 cm. (the light passing through a plate glass window), produced only a 10% increase in velocity, a result which suggests that the effect of diffused daylight would be very small.

In the experiments detailed in this second paper, Gilbert used the following solutions at 25° C. :—40 c.c. potassium ferricyanide solution (0·04 or 0·08 molar), 40 c.c. hydrazine sulphate solution (0·01 or 0·02 molar), and 20 c.c. disodium phosphate solution (0·2 molar). He noted that phosphate in this concentration did not buffer the solution completely, since five hydroxyl ions are used up for each molecule of hydrazine oxidized. The diminution in velocity of the reaction is therefore greater than would be expected from the fall in concentration of the hydrazine or ferricyanide. The mixture in Gilbert's experiments was stirred at 250 r.p.m., and the progress of the reaction followed by collecting the nitrogen over mercury at atmospheric pressure.

The writers considered it advisable, before seeking inhibitors, to re-examine the course of the uninhibited reaction.

Reagents and Apparatus.

Merck's hydrazine sulphate was employed, and the potassium ferricyanide was recrystallised before use.

In the majority of the experiments, the apparatus used was somewhat similar to that employed by Gilbert. The reaction chamber was a glass bottle. This was coated on the outside with black paint, although experiment showed that, as suggested above, the error involved by not excluding light was very small. Through the trebly-bored rubber stopper of the reaction bottle passed a tube for addition of reagents, a tube connected to the constant pressure gas burette, and a mercury-sealed stirrer consisting of a T-piece of glass tubing joined to a glass rod. The arms of the T-piece, which were immersed in the

liquid, were left open, and a hole was blown above liquid level close to the joint with the glass rod. When the stirrer is rotated sufficiently rapidly, gas from the upper part of the vessel enters at this hole, and sprays out through the arms of the T-piece. Thus the liquid is not only violently agitated, but in addition a constant stream of bubbles is pumped through it, so that tendency to gaseous supersaturation might be expected to be small.

Results and Discussion.

The reaction mixture used was:—40 c.c. 0·04 molar potassium ferricyanide solution, 20 c.c. 0·2 molar disodium phosphate solution, and 40 c.c. 0·01 molar hydrazine sulphate solution. The final reagent was added with the stirrer running. As quickly as possible after adding it, the apparatus was made gas-tight and readings commenced. A little nitrogen is lost during the introduction of the final reagent, and perfectly concordant results were not obtained, so an average value was taken from a considerable number of experiments. No correction was made for variation in atmospheric pressure, since the experiments did not seem accurate enough to justify the correction. The possible yield of nitrogen was 8·96 c.c. at standard temperature and pressure.

In a set of preliminary experiments, performed without stirring, the rate of evolution of gas was much slower than that reported by Gilbert, and substitution of nitrogen for air in the reaction vessel did not make any appreciable difference. When the solution was stirred, much higher rates of evolution of gas were obtained, and it was soon discovered that they depended markedly on the rate of stirring.

Experiments at 25° C.

Stirring rate (revolutions per minute).	Volume of gas (in c.c.) evolved at times in minutes given in first line.											
	1	2	3	4	5	6	7	10	11	15	20	25
150	0·2		0·7		1·1		1·65		2·75	3·7	4·6	
250	0·3		0·95		1·65		2·4	3·45		4·9	6·15	7·2
500	0·55	1·35	2·15	2·8	3·5	4·1	4·55	6 0		7·05		
900	1·9	3·8	5·1	6·0	6·5	7·1	7·4					
1300	2·5	5·2	6·2	6·8	7·2	7·4						

The rates recorded by Gilbert (stirring at 250 r.p.m.) agree most nearly with our rates for 150 r.p.m. Of course, not only the rate of stirring, but also the efficiency of the stirrer, would affect the results. The gas evolved was analysed, and appeared to be pure nitrogen.

The simplest explanation of the dependence of the rate at which gas was evolved on the rate of stirring seemed to be that there was a tendency for the

solution to become supersaturated with nitrogen. It was at once apparent that this involved the retention in the unstirred or slowly stirred solution of five times as much nitrogen as could be accounted for by the normal solubility of the gas (about 1·4 per cent. in water at 25° C.), a conclusion which seemed so improbable that the writers at first rejected this explanation. Other possibilities were (1) that reaction takes place at the glass surface of the vessel, diffusion to which is hastened by stirring, (2) that reaction takes place at the liquid-gas interface, which interface is greatly increased by rapid stirring with bubble formation, (3) that the reaction is retarded by the nitrogen produced, unless this is quickly removed.

The rate of evolution of gas was almost doubled by the addition of glass beads of total surface equal to that of the original vessel. This result was compatible with (1) above, but could also be explained on a supersaturation theory, the additional solid surface providing extra points from which the gas could escape from solution. Explanation (2) was ruled out by an experiment in which a long narrow tube with similar glass surface but only one-fifth the liquid-gas interface was substituted for the original reaction vessel. The same rate of evolution of gas was observed. Explanation (3) was rendered unlikely by the fact that experiments in which nitrogen had been substituted for the air initially present in the reaction vessel had not given a materially different result.

The writers then decided to examine the supersaturation explanation. If supersaturation actually occurs, there are two possibilities:—(*a*) the reaction is really instantaneous, and we merely measure the rate at which nitrogen can be removed by stirring, (*b*) the reaction is not instantaneous, but is so rapid that stirring even at 1300 r.p.m. can scarcely remove the nitrogen as fast as it is formed. To test possibility (*a*) the reaction was carried out at 0°. If the reaction is instantaneous at 25° it would probably be instantaneous at 0° also, while if it requires a finite time at 25° it should be much slower at 0°. By immersing the reaction vessel in melting ice, it was found that, at 0° also, the stirring rate governed the rate of evolution of gas. It is obvious from the results given below (the average of a number of experiments) that the reaction at 0° is much slower than at 25°.

Experiments at 0° C.

Stirring rate (revolutions per minute).	Volume of gas (in c.c.) evolved at times in minutes given in first line.					
	1	2	5	10	15	20
500	0·2	0·3	0·35	0·5	0·6	0·9
900	0·2	0·4	0·6	1·4	1·55	1·85

These results render the theory of instantaneous reaction very improbable.

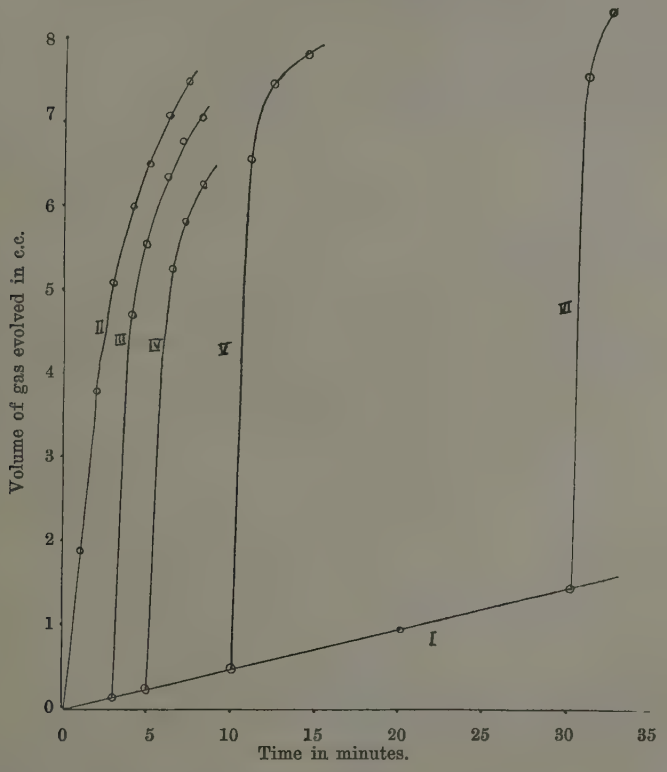
Conclusive evidence in favour of possibility (*b*) was obtained when experiments were performed in which the reaction was allowed to proceed for

some time without stirring, and vigorous stirring was then commenced. Rapid evolution of gas occurred, and the total volume evolved soon equalled that which would have been obtained if the solution had been stirred from the beginning. For example, a solution was left unstirred for 10 minutes, and stirring at 900 r.p.m. was then commenced:—

Experiment with Stirrer Started at End of 10 Minutes.

Stirring rate (revolutions per minute).	Volume of gas (in c.c.) evolved at times in minutes given in first line.					
	4	8	10	11	12	14
900	0·3	0·5	0·55	6·5	7·4	7·75

The results are summarized in the accompanying figure.



Graph I.—Solution unstirred.
Graph II.—Solution stirred from start.
Graphs III–VI.—Stirring commenced after 3, 5, 10, and 30 minutes respectively.

The rates of evolution of nitrogen in Experiments III, IV, V, and VI, were 4·5, 4·9, 5·95, and 6·15 c.c. respectively in the first minute of stirring.

It seems clear that in all cases the reaction proceeds at a rate independent (or nearly so) of stirring, and that at any time the greater part of the nitrogen produced up to that point can be rapidly liberated if sufficiently vigorous stirring is applied.

Supersaturation of Liquids with Gases.

Text-books on general or physical chemistry sometimes mention the fact that liquids may be supersaturated with gases, just as with solids, but the writers have not found in any text-book quantitative information, nor any suggestion that gaseous supersaturation can take place to an extent unknown with solid solutes.

Experiments were made to see if supersaturation occurs in other cases of mixtures which evolve a gas. Results very similar to those for hydrazine oxidation were obtained with a mixture of 75 c.c. M/100 hydrogen peroxide solution, and 25 c.c. N/8 sodium hydroxide solution. With a stronger hydrogen peroxide solution results were obtained which indicated that 14 c.c. of oxygen must have been in supersaturated solution in 100 c.c. of liquid. Similarly, using a reaction mixture of 40 c.c. of 0·16 molar $K_3Fe(CN)_6$, 20 c.c. of 0·4 normal NaOH, and 40 c.c. of 0·04 molar hydrazine sulphate, it was found that up to 20 c.c. of nitrogen might remain in solution in excess of the normal solubility. This is fourteen-fold supersaturation.

It was discovered at this point that several papers on gaseous supersaturation (not yet cited by the text-books) have been published. K. S. Wyatt (Trans. Roy. Soc. Canada, (iii), **18**, 127, 1924) found that an aqueous solution of nitrogen saturated at a pressure exceeding 100 atmospheres at air temperature could be brought to atmospheric pressure without the immediate formation of bubbles in the liquid, and Kenrick, Wismer, and Wyatt (J. Phys. Chem., **28**, 1308, 1924) obtained similar results with oxygen, nitrogen, and carbon dioxide. About the same time Metschl (J. Phys. Chem., **28**, 417, 1924) investigated the supersaturation of water and various organic liquids with oxygen, nitrogen, hydrogen, and carbon dioxide, at five atmospheres pressure, and found that the resulting solutions were very stable at atmospheric pressure, vigorous agitation being required before all the excess gas could be removed. Metschl summarizes in a few references the previous work on the subject, almost all being only qualitative.

A letter from the writers in *Nature* (**131**, 762, 1933) called attention to the importance of the above-mentioned papers, which appear to have received less notice than they deserve. At the same time the validity of the results obtained by Gilbert on the rate of decomposition of hydrazine was questioned. After the appearance of this letter a further paper—not given by Metschl in his list of references—on supersaturation of liquids by gases was discovered. F. E. E. Lamplough (Proc. Cambridge Phil. Soc., **14**, 580, 1908) approached the question

from the point of view of determination of rate of chemical change by measurement of gases evolved. He investigated such reactions as that of nickel carbonyl and iodine producing carbon monoxide, decomposition of hydrogen peroxide, of diazobenzene chloride, of formic acid by sulphuric acid, and of urea by sodium hypochlorite. In each case he found that supersaturation occurs unless overcome by adequate means. In some experiments, in which nitrogen was the gas evolved, the degree of supersaturation was so great that the solvent contained more than 100 times the normal amount of gas. He also investigated the connection between rate of evolution of gas and degree of supersaturation by means of experiments performed with and without stirring. In particular, he showed the earlier work of Hantzsch (Ber. **33**, 2517, 1900) and Cain and Nicholl (J. Chem. Soc., 1412, 1902) on the kinetics of the decomposition of diazobenzene chloride to be quite misleading, since these workers had taken no steps to overcome supersaturation. It is interesting also to recall that Berthelot (Ann. Chim. Phys. (5), **21**, 176, 1880) suggested the existence of a higher oxide of hydrogen, such as H_2O_3, on the strength of an observation that when potassium permanganate reacts with hydrogen peroxide at low temperatures, the permanganate is decolorized without liberating oxygen. That this was due to supersaturation of the solution by oxygen was pointed out by von Baeyer and Villiger (Ber., **33**, 2488, 1900).

Summary.

When hydrazine is oxidized by potassium ferricyanide in alkaline solution, supersaturation of the solution by nitrogen takes place so readily, and to such an extent, that the rate of evolution of nitrogen can only be used to follow the course of the reaction if stirring is very efficient.

Attention is drawn to previous investigations of gaseous supersaturation, to the general occurrence of this phenomenon, and to the ease with which it may invalidate quantitative work on chemical kinetics.

Part II: The Reaction in Presence of Acetone.

The discrepancies in apparent velocity of reaction having been explained (Part I), the search for inhibitors was begun.

In all experiments the temperature was 25° C., and the rate of stirring 900 r.p.m., possibly not high enough to give the maximum rate of evolution of gas, but sufficiently high for comparative experiments. Experiments were performed with the following reaction mixture:—40 c.c. 0·01 molar hydrazine sulphate, added to 20 c.c. 0·08 molar potassium ferricyanide, 20 c.c. 0·2 molar disodium phosphate, and 20 c.c. 0·02 molar phenol or acetone. Neither of these substances, in this concentration, produced much alteration in rate. When, however, the strength of the acetone solution was increased, retardation of the reaction was observed, and the remainder of the paper is concerned with this phenomenon.

The ferricyanide, phosphate, and acetone solutions were mixed and allowed to come to the temperature of the thermostat, the hydrazine sulphate solution being added last. It was found, for example, when the final reaction mixture was M/10 with respect to acetone, that, although the reaction was initially vigorous, it came almost to a standstill when about half the theoretical amount of gas had been evolved, and that even after a considerable time (two or three days) the calculated amount of gas (8·96 c.c. at S.T.P.) was not evolved. In these experiments, some of which lasted for several days, corrections were made for the effect of the changes in atmospheric pressure on the volume of the air originally present in the apparatus. The following table shows a few typical results:—

Acetone concentration in final mixture.	Volume of gas (in c.c.) evolved at times given in first line.					
	2 min.	5 min.	10 min.	100 min.	22 hrs.	80 hrs.
0·017 molar	2·05	4·8	6·3	7·45		
0·086 molar	2·1	3·8	4·2		7·45	
0·10 molar	2·0	3·45	3·5			5·1
0·82 molar	nil.	nil.	nil.		0·5	

It will be seen that, at the highest concentration of acetone employed, evolution of gas was almost completely suppressed. The explanation which immediately suggested itself was that the acetone was reacting with hydrazine to form a hydrazone or a ketazine, and so preventing its oxidation by ferricyanide. This hypothesis was supported by experiments in which the order of mixing was altered, the hydrazine solution being placed with the acetone and the buffer in the reaction bottle, and left for a short time before the ferricyanide was added as final reagent. The hydrazine and acetone might now be expected to have reacted before the addition of the ferricyanide, so that the inhibition would be more marked. This was found to be the case. For example, in an experiment in which the concentration of acetone was 0·12 molar, gas was liberated at the rate of about 0·2 c.c. per hour, and the volume only reached 5 c.c. in about two days.

Before accepting this explanation, certain points demanded investigation:—

(1) One might suppose that a hydrazone or ketazine thus formed would be attacked by potassium ferricyanide in much the same way as hydrazine.

(2) Gilbert (J. Amer. Chem. Soc., **51**, 3394, 1929) has demonstrated the existence of an equilibrium, discussed later in more detail, between hydrazine, acetone, and their condensation products, and one might expect that the removal of free hydrazine by oxidation would upset this equilibrium, that more hydrazine

would be liberated and oxidized, and that the reaction would proceed rapidly to completion.

(3) It is possible that, in presence of acetone, the course of the reaction might be profoundly altered, and the nitrogen of the hydrazine, instead of being set free as nitrogen gas, might appear in some other form such as ammonia. Alternatively, autoxidation of hydrazine, although insignificant in the absence of acetone (Part I) might become important in its presence.

The solutions from (*a*) an uninhibited, and (*b*) a heavily inhibited reaction, were made alkaline and distilled, ammonia being estimated in the distillate by means of Nessler's reagent. The amounts found corresponded to (*a*) 1·7 per cent., (*b*) 4·2 per cent. of the total nitrogen. Although this shows an increase in ammonia production in presence of acetone, the amount formed is quite inadequate to explain the deficient yield of nitrogen in presence of acetone.

The possibility was also investigated that, when the reaction is slowed down, the hydrazine is attacked by oxygen, from the air in the apparatus, or dissolved in the solutions.

$$N_2H_4 + O_2 = 2H_2O + N_2.$$

Since the oxygen used up would be equal in volume to the nitrogen produced, a deficiency in yield of gas would result. Experiments were performed in a nitrometer, in which air was excluded and the solutions were made with water previously boiled and cooled in a current of nitrogen. Since ferricyanide attacked the mercury in the nitrometer, slight excess of this reagent was used. In absence of acetone the reaction gave a quantitative yield of gas, but in presence of acetone great retardation took place and the full yield of gas was not obtained. Exclusion of air seemed to make no appreciable difference to the reaction.

Gradual addition of ferricyanide was also tried, in consequence of a suggestion that ferricyanide might tend to oxidize acetone hydrazone (if formed) to a more stable tetrazone, and that, if only sufficient ferricyanide to react with free hydrazine were added at one time, all the hydrazine might be oxidized to nitrogen. No improvement in yield was observed when this was tried.

It was found, however, that if the solution in the nitrometer was acidified with sulphuric acid when evolution of gas ceased, and after about thirty minutes made alkaline with caustic soda, a further volume of gas was obtained. By repeating this process three times a volume of gas amounting to 90 per cent. of the theoretical was obtained. This can be explained on the theory that a ketazine is present, and that in acid solution it is hydrolysed to hydrazine which, on addition of alkali, is oxidized by ferricyanide before it can revert to ketazine.

A search was now made for a method of volumetric analysis by which the results obtained by the gasometric method might be checked. Unfortunately, all methods for titration of hydrazine depend on its reducing properties, and since for each molecule of hydrazine destroyed in our reaction mixture an equivalent amount of ferrocyanide is produced, the amount of reducing material

remains constant during the reaction. If, however, the hydrazine combines with acetone to form a substance without reducing properties, the reaction mixture inhibited with acetone would contain less reducing material than when acetone is not present.

One of the simplest and best methods of estimating hydrazine is by means of iodine in alkaline solution (Bray and Cuy, J. Amer. Chem. Soc., **46**, 863, 1924). This was the method used throughout in checking the hydrazine sulphate solutions, but it is clearly not applicable in presence of acetone, since iodoform would be produced. Another method found satisfactory by Bray and Cuy was the use of bromine in acid solution as the oxidizing agent. It was found that, within the limit of experimental error, no hydrazine was prevented by acetone from being oxidized by bromine. The same was true of oxidation by potassium dichromate in acid solution. Since, however, dimethylketazine, if formed under the experimental conditions in slightly alkaline solution, would no doubt be hydrolysed on addition of acid, these agents which operate in acid solution cannot be expected to differentiate between combined and uncombined hydrazine.

One titration method was devised which, although not distinguishing between combined and free hydrazine, enabled the rate of oxidation of hydrazine by ferricyanide to be followed independently of the evolution of nitrogen. It consisted in titrating with potassium permanganate. Ferrocyanide reacts quantitatively with permanganate in acid solution

$$2KMnO_4 + 10K_4Fe(CN)_6 + 8H_2SO_4 = 10K_3Fe(CN)_6 + 6K_2SO_4 + 2MnSO_4 + 8H_2O$$

but the oxidation of hydrazine is not exactly represented by the equation

$$4KMnO_4 + 5N_2H_5HSO_4 + H_2SO_4 = 2K_2SO_4 + 4MnSO_4 + 16H_2O + 5N_2.$$

This has long been known, and many investigations have been carried out on the problem. A satisfactory explanation was given by Cuy, Rosenberg, and Bray (J. Amer. Chem. Soc., **46**, 1796, 1924), who claimed that the presence of manganous salt formed during the reaction is responsible for the fact that the amount of oxidizing agent required to oxidize one mole of hydrazine is variable and much lower than the expected four equivalents, falling as low as 1·45 in the presence of excess manganous salt. Designating the number of equivalents by the letter *R*, they found it to lie between 1 and 2 when the hydrazine and permanganate were titrated directly against one another in sulphuric acid solution. For ferrocyanide, however, *R* has the obvious stoichiometric value. *R* for hydrazine in the concentration used in these experiments was found to be 1·72 when titration was carried out with N/10 $KMnO_4$ in strongly acid solution.

The progress of the reaction was now investigated by withdrawing 25 c.c. samples at intervals, running the sample into 25 c.c. N – H_2SO_4, and titrating with N/10 $KMnO_4$. In the acid solution further reaction between hydrazine and ferricyanide would be greatly retarded. 25 c.c. of the reaction mixture

originally contained 10 c.c. of 0·01 molar hydrazine, which would require 1·72 c.c. permanganate. Since each molecule of hydrazine on oxidation produces four molecules of ferrocyanide, the ferrocyanide produced by the complete oxidation of the hydrazine would require 4 c.c. permanganate.

If x = percentage hydrazine remaining at any time

and y = permanganate titre,

then $$\frac{1{\cdot}72x + (100 - x)\,4}{100} = y.$$

The following results show an agreement with the gasometric method which is fairly close, considering the velocity of the reaction, and the difficulty of removing nitrogen from solution sufficiently rapidly :—

Time of withdrawal (minutes).	Permanganate titre (c.c.).	x	Corresponding vol. of nitrogen at S.T.P. (c.c.).	Vol. evolved with stirring at 900 r.p.m. (c.c.).
1	2·25	76	2·1	1·9
2	2·9	48	4·7	3·8
3	3·1	39	5·5	5·1
5	3·6	17	7·5	6·5
8	3·75	11	8·0	7·7
10	3·8	9	8·2	
20	3·95	2	8·8	
50	3·95	2	8·8	

If the mixture was made M/10 with respect to acetone, after 30 minutes the reaction, as followed by the permanganate method, was only 59 per cent. complete when hydrazine was the final reagent, and only 28 per cent. complete when ferricyanide was added last.

Similar results were obtained by a colorimetric method. Standards were made up with suitable proportions of 0·04 molar ferricyanide and 0·04 molar ferrocyanide to imitate the composition of the reaction mixtures at various stages of the reaction. The correct amount of disodium phosphate (and acetone, when comparing with an inhibited reaction) was also added. The yellow colour becomes paler as the proportion of ferricyanide decreases. Comparisons were made by means of the actual solution colour, and also by means of the colours obtained by diluting the solutions one-hundred-fold, and adding a few drops of copper sulphate solution. With the ordinary reaction the rate was approximately the same as that found by the gasometric method, and with acetone present the reaction did not go to completion.

These methods of analysis confirmed the belief that the gasometric method furnishes reliable evidence as to the rate of oxidation of hydrazine, whether acetone is present or not.

The above experiments prove fairly definitely that in presence of acetone hydrazine is not quantitatively oxidized to nitrogen by ferricyanide, at least within a reasonable time, that it is not extensively oxidized to any other nitrogenous product, and that the reaction comes to an end while there is still ferricyanide present.

Since the original preparation of acetone hydrazone, $(CH_3)_2C:N.NH_2$ (Curtius and Pflüg, J. pr. Chem., **44**, 543, 1891), and of dimethylketazine $(CH_3)_2C:N.N:C(CH_3)_2$ (Curtius and Thun, J. pr. Chem., **44**, 164, 1891), little work seems to have been done on these compounds apart from the paper by E. C. Gilbert already mentioned (J. Amer. Chem. Soc., **51**, 3394, 1929). He investigated the hydrolysis of dimethylketazine, and the equilibrium between hydrazine and acetone in aqueous solution. He considered that a state of equilibrium was reached which may be represented by the following reversible equations:—

$$(CH_3)_2C:N.N:C(CH_3)_2 + H^+ + H_2O = (CH_3)_2C:N.NH_3^+ + (CH_3)_2CO, \quad (1)$$

followed by

$$(CH_3)_2C:N.NH_3^+ + H_2O = N_2H_5^+ + (CH_3)_2CO. \quad (2)$$

An explanation on these lines is subject to a difficulty already propounded that, as hydrazine is removed by oxidation, one would expect more ketazine or hydrazone to break up, so that eventually all the hydrazine would be set free for oxidation. In addition, our reaction mixture tends to contain more hydrogen ions as hydrazine is destroyed and so equilibrium (1) should move more to the right.

Gilbert determined the equilibrium constant of reaction (2), K_2, by two different methods, one of which depended on the distribution of acetone between benzene and an aqueous solution of hydrazine salt. The solution was made sufficiently acid to prevent the formation of ketazine. The actual calculation of the constant in the table on p. 3399 of Gilbert's paper seems to us to be open to objection, as the amount of acetone in the benzene layer appears to be ignored. The principle of the method is, however, sound, and experiments on these lines were made to test whether under our conditions hydrazine and acetone react with compound formation.

Evidence was obtained that more than half the acetone in the aqueous layer had reacted with hydrazine when the following solutions were shaken at room temperature for some time:—20 c.c. 0·07 molar acetone solution, 20 c.c. 0·2 molar disodium phosphate solution, 40 c.c. 0·02 molar hydrazine sulphate solution, and 25 c.c. benzene. Acetone was estimated in the benzene layer by Messinger's method (reaction with iodine in alkaline solution, followed by thiosulphate titration in faintly acid solution of the surviving iodine).

The result showed qualitatively that acetone and hydrazine react under the conditions of our experiments. A similar experiment in which the hydrazine-ferricyanide reaction was allowed to take place in presence of acetone indicated that hydrazone and (or) ketazine were present after the reagents had been left together overnight, and the low concentration of hydrogen ions in our experiments makes it likely that dimethylketazine rather than acetone hydrazone is the chief condensation product formed. It seemed probable that when the reaction took place in the presence of acetone, since the hydrolysis of ketazine requires an acid solution and the oxidation of hydrazine by ferricyanide an alkaline solution, the point at which the reaction comes to a virtual standstill is that at which the concentration of free hydrazine becomes so low and its replacement from the ketazine so slow that its oxidation gives rise to an almost infinitely slow evolution of nitrogen.

Dimethylketazine was prepared by the method of Curtius and Thun (J. pr. Chem., **44**, 164, 1891). Hydrazine hydrate solution was produced by mixing boiling solutions of equimolecular proportions of hydrazine sulphate and barium hydroxide. The barium sulphate was filtered off, and the solution fractionated under atmospheric pressure. An approximately 50 per cent. solution was eventually obtained. This was gradually added to a quantity of acetone (in excess of the two molecules required by the equation) cooled by a freezing mixture. The liquid was shaken with solid caustic potash, and the lighter layer fractionated. The final fraction, boiling at 130° (uncorr.) was retained. (B.P. dimethylketazine = 131°.) An approximately 0·05 molar solution of dimethylketazine was prepared. A portion was hydrolysed in acid solution, and the hydrazine estimated by the iodic acid method (Bray and Cuy, J. Amer. Chem. Soc., **46**, 859, 1924). The solution titrated as containing 98·9 per cent. of the ketazine weighed out.

Experiments were carried out on the oxidation of this ketazine solution with ferricyanide in a nitrometer, with shaking.

I. 5 c.c. ketazine solution, 10 c.c. 0·2 molar disodium phosphate solution, 6 c.c. 0·2 molar potassium ferricyanide solution. (Theoretical yield of nitrogen = 5·83 c.c.) After two days 5·74 c.c. of nitrogen had been evolved. II. As above with the addition of 0·2 c.c. of acetone to the ketazine solution. After five days, 3·03 c.c. of nitrogen were evolved.

III. 5 c.c. ketazine solution, 5 c.c. normal sodium hydroxide solution, 10 c.c. 0·2 molar potassium ferricyanide solution. After four days, 1·80 c.c. of nitrogen had been evolved.

These experiments show that, while nitrogen is evolved almost quantitatively, though slowly, from a ketazine solution by the action of ferricyanide under our experimental conditions, the addition of an excess of acetone renders the oxidation extremely slow, presumably by retarding hydrolysis of the ketazine. In strongly alkaline solution, even in absence of acetone, oxidation is greatly retarded, presumably because hydrolysis of ketazine takes place very slowly in the almost complete absence of hydrogen ions.

Summary.

When acetone is present in considerable excess, the oxidation of hydrazine by potassium ferricyanide in a solution buffered with disodium phosphate is slow and incomplete.

This retardation is caused mainly by the formation of dimethylketazine. Potassium ferricyanide is apparently unable to oxidize dimethylketazine until the latter has been hydrolysed to hydrazine. This hydrolysis takes place very slowly under the experimental conditions.

Since the hydrolysis of dimethylketazine requires hydrogen ions, and the oxidation of hydrazine by potassium ferricyanide requires hydroxyl ions, it is impossible to secure conditions under which hydrolysis and oxidation proceed simultaneously and rapidly.

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